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The Hydrodynamic Solution for Flow Profiles in a Binary Strong Electrolyte Solution Under an External Electric Field

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Abstract

In this paper, we follow the general idea of the Onsager–Wilson theory of strong binary electrolyte solutions and completely calculate the velocity profile of ionic flow by first formally solving the hydrodynamic (Stokes) equation for the ionic solutions subjected to an external electric field by a Fourier transform method and then explicitly evaluating the formal Fourier transform solutions as functions of spatial positions and field strength. Thus the axial and transversal components of the velocity and the accompanying nonequilibrium pressure are explicitly obtained. They are rare examples for solutions of a hydrodynamic equation for flow in an external electric field. The present results make it possible to investigate ways to overcome the mathematical difficulty (divergence) inherent to the method of evaluating the formal solutions that Wilson used in his dissertation on the conductance theory (namely, the Onsager–Wilson theory) for strong binary electrolytes. Some examples for the velocity profiles are numerically computed. They show how ions might move in the ionic solution under an external electric field. A possible way to get rid of the divergence causing terms for the electrophoretic effect is examined. In the sequels, the results obtained in this work will be applied to study ionic conductivity and related transport processes in electrolyte solutions.

I. Introduction

The principal initial motivation for study underlying this work was in our desire to benefit from Onsager's theories of conductance of electrolyte solutions which should be quite relevant to various subjects in the fields of transport phenomena in plasmas,^{1,2,3} ionic systems^{4,5,6,7} and semiconductors^{8,9,10} and micro and nano systems^{11,12,13} consisting of electrolyte solutions and plasmas, since the conductivity and mobility of charged species subjected to external electromagnetic fields are of great interest regardless of the scales of the system size. At quick glance, one might think that Onsager's theories^{14,15} on the subject matter appear dated at first glance, but the present authors believe there are some features that are still as relevant and significant even today as before. In pursuing this line of study we have learned that there are things of importance to improve on or extend in his theory of electrolyte conductance and new avenues to explore as improvement and extension unfold, as will be discussed in the course of this line of study.

In the study of ionic conductivity, one is interested in currents carried by ions in solution subjected to an external electric field not necessarily weak. As the field strength increases, the conduction current has been observed to deviate from the Ohmic law prediction. We in fact observe the well-known Wien effect,¹⁶ which is a non-Ohmic conductance of electrolyte solutions subjected to high external applied electric field¹⁷ that defy a linear theory description. Currently, such non-Ohmic phenomena are generally observed, for example, in semiconductors^{8,9,10,11} and expected to be operative in micro and nanosystems because of the necessarily large field gradients in such systems. Onsager's theory is judged to provide valuable insights despite the differences in the sizes and states of aggregation of the systems and hence worth a serious study.

The general ideas underlying conductance in ionic solutions, which originally

was Onsager's,¹⁴ consist of two effects: one is the electrophoretic effect and the other the relaxation time effect. These can be heuristically and qualitatively understood as follows: Let the force on ion j be

$$\mathbf{k}_j = e_j \mathbf{X} \quad (j = 1, \dots, s) \quad (1)$$

with \mathbf{X} denoting the external electric field and e_j the charge of ion j . The ion of charge e_j in the solution will possess an ionic atmosphere of charge $-e_j$, and this atmosphere will be subjected to a force of $-e_j \mathbf{X}$. This force will tend to move the atmosphere in the direction of force $-e_j \mathbf{X}$, while the central ion j will be carried in the medium in a direction opposite to the motion of ion atmosphere. The velocity of this *countercurrent* may be readily calculated if it is assumed that the entire charge $-e_j$ of the atmosphere is distributed in a spherical shell of radius κ^{-1} from the central ion and that the motion of this sphere is governed by the Stokes law^{19,20} holding for the motion of a sphere in a viscous fluid. Thus, this velocity of the countercurrent is estimated to be

$$\Delta \mathbf{v}_j = -\frac{\mathbf{k}_j \kappa}{6\pi\eta} = -\frac{e_j \mathbf{X} \kappa}{6\pi\eta}, \quad (2)$$

where $\Delta \mathbf{v}_j$ is the velocity of the interior of the shell and η_0 is the viscosity of the medium. We are thus led to the result that the medium in the interior of the shell will be travelling with this velocity, and that the central ion will migrate against a current of this magnitude. The deduction of this expression qualitatively elucidates the most important part of the effect of electrophoresis. One may improve upon it by means of a hydrodynamic method using the Navier-Stokes equations.

The second effect is: if the central ion possessed no atmosphere it would migrate with a velocity \mathbf{k}_j/ζ_i (ζ_i = friction constant), but owing to its atmosphere, the ion is subjected to a force, $\mathbf{k}_j - \Delta \mathbf{k}_j$, where $\Delta \mathbf{k}_j$ is the force arising from the dissymmetry of the ion atmosphere created by the movement of the ion, and

hence it will move with a velocity, relative to its environment, of a magnitude, $(\mathbf{k}_j - \Delta\mathbf{k}_j)/\zeta_j$. Consequently, the net velocity \mathbf{v}_j of ion j is given by

$$\mathbf{v}_j = \frac{(\mathbf{k}_j - \Delta\mathbf{k}_j)}{\zeta_j} + \Delta\mathbf{v}_j. \quad (3)$$

For the case of electrical conduction, we obtain

$$\mathbf{v}_j = \frac{(e_j\mathbf{X} - \Delta\mathbf{k}_j)}{\zeta_j} - \frac{e_j\mathbf{X}\kappa}{6\pi\eta}. \quad (4)$$

Here $\Delta\mathbf{k}_j\zeta_j^{-1}$ represents the relaxation time effect. The aforementioned two effects underlie a qualitative explanation of the electrophoretic and relaxation time effects in conduction.

The Onsager–Wilson (OW) theory²¹ is a theory of conductance of strong binary electrolyte solutions in an externally applied electric field. It formally calculates the ionic conductances by using the Onsager–Fuoss (OF) equations¹⁵ for distribution functions and the Poisson equation²² for the modification of the field $\Delta\mathbf{k}_j$ by the presence of the ion atmosphere and, in addition to the aforementioned two equations, the Navier–Stokes (NS) equation²³—more precisely, Stokes equation—for the velocity of the medium to calculate the electrophoretic effect. Henceforth the NS equation refers to the Stokes equation in this article. For the NS equation the local body force arising from the external electric field and many-body effects must be calculated from the statistical mechanics (kinetic theory) of electrolyte solutions. In the OW theory the local body force is calculated from the solutions of the OF and Poisson equations. The OF equations are coupled differential equations for pair distribution functions of ions in the electrolyte solution, which are Fokker–Planck type equations for ions moving like Brownian particles in the solution subjected to an electric field. It is useful to note that, although the OF equations were originally assumed on physical grounds they can be derived by means of the kinetic theory of dense fluids if a Brownian motion model is assumed and the many-particle distribution function

is suitably approximated.²⁴

In his 1936 Yale University dissertation under the supervision of L. Onsager, W. S. Wilson²¹ presented a formal solution for the NS equation obtained by means of the method of Fourier transforms with the local body force determined from the OF and Poisson equations. The formal solution consists of sine and cosine transforms of rather complicated functions. Since the external field is assumed directed in the positive x direction of the coordinate system and there is an axial symmetry around the x axis, the natural coordinates are cylindrical coordinates (x, ρ, θ) , where x is the axis of the cylinder, ρ is the radial coordinate perpendicular to the cylinder axis, and θ is the azimuthal angle in the plane perpendicular to the x axis—parallel to the field direction. See Fig. 1 for the coordinates defined. The solution therefore is axially symmetric and hence does not depend on angle θ . The formal Fourier transform solution for the NS equation obtained thereby, however, must be more explicitly calculated as a function of x and ρ to make further progress in theory. Unfortunately, the Fourier transform solution is not a kind that can be easily evaluated in elementary functions since it consists of rather complicated integrals. Wilson considered a special case of position coordinates for evaluation of the Fourier transform solution.

Since the ion j of ion atmosphere is the object of attention and is assumed located at the center of the ion atmosphere, which is taken to be at the coordinate origin, he sets $x = 0$ and $\rho = 0$ in the integrals making up the solution, which then become amenable to exact and analytic evaluations. But there is one integral among them that clearly gives rise to divergence making the choice of $x = 0$ and $\rho = 0$ inappropriate.

Despite his argument to the effect that it does not contribute to the solution because its contour integral vanishes, it is reasonable to say in retrospect that

he simply discarded the divergent term and retained only the convergent integrals for the calculation of electrophoresis. Despite this troublesome aspect, the result of such a calculation was subsequently entrenched in the literature¹⁸ on conductance of electrolyte solutions, especially, in connection with the Wien effect on the ionic conductance. We find that, mathematically, this difficulty arises because some of the integrals involved in the Fourier transform solution are not uniformly convergent for all values of the position coordinates. For this reason it is not possible to set $x = 0$ and $\rho = 0$ in some of the integrals before their integrations are fully performed.

We, in fact, will find that, when exactly evaluated, some of the integrals give rise to functions diverging as x and ρ approach to the coordinate origin. In other words, the solution of the NS equation for the velocity is inherently singular at the origin of the coordinate system. It then becomes crucially important to re-examine the OW theory to get around this difficulty and suitably revise it before making use of it to interpret experiments on conductance, because there arises the question of what is really meant by the electrophoretic effect and conductance calculated therewith, given a velocity distribution that depends on x and ρ and is manifestly divergent as $x, \rho \rightarrow 0$.

In this work, we avoid Wilson's procedure²¹ of setting $x = 0$ and $\rho = 0$ within the integrals before they are evaluated, yet manage to completely evaluate them analytically or reduce them to easily computable quadratures. Thus we obtain relatively much simpler velocity formulas than the Fourier transform solution that explicitly depend on x and ρ as well as the field strength, for the axial and transversal velocities and the nonequilibrium part of pressure nonlinearly depending on the external field strength. As a matter of fact, the results obtained for the velocities and pressure appear to be rare examples for the solutions of the NS equation of a fluid (e.g., electrolytes) in an external electric

field when the flow is laminar that is applicable to practical experimental situations. The velocity profiles obtained display the manner in which the ions move in the applied electric field, and there is much insight to be gained with regard to the mode of ionic conduction in electrolyte solutions. In the sequels to this work, we will investigate its application to studies of ionic conductance and other transport processes in ionic solutions.

This article is organized as follows. In Sec. II, the formal (Fourier transform) solutions of the OF equations for pair distribution functions and the Poisson equations for potentials are briefly reviewed to provide the basis for the local body force—an electric field in the present case—that is necessary for the NS equation for velocity of the electrolyte solution in an external electric field. The solutions of the OF and Poisson equations are those of Wilson’s in his dissertation, which have been also presented in a recent tutorial review article²⁶ by one of the present authors. In Sec III, the solution of such an NS equation was formally solved in the same manner as by Wilson. We repeat his formal solution procedure, because his work has never been published, only a brief summary of the pertinent results having been given in the monograph of Harned and Owen¹⁸ and in the review article by Eckstrom and Schmeltzer.²⁷ His thesis²¹ itself not only skips details of the solution procedures used, making it difficult to follow, but also contains some errors, typographical or otherwise, in some important steps and results. Moreover, as mentioned earlier, some of the integrals making up the formal solution diverge at the origin of the coordinate system, causing difficulty to ascertain the true nature and meaning of the electrophoretic effect deduced in his dissertation. For this reason, in this work we will solve the NS equation afresh, which by itself is quite worthwhile to learn about for its pedagogical value for those not well versed in fluid dynamics of ionic solutions. In Sec. IV, the formal solution consisting of a number of Fourier transforms of

complicated integrands including Bessel functions²⁸ of complicated arguments will be explicitly evaluated by using the method of contour integrations.²⁹ We thereby obtain explicit velocity profiles as functions of coordinates and field strength for axial and transversal flows of the electrolyte solution in a coordinate system fixed at the center ion of ion atmosphere. Therefore the velocity profiles are of the medium with countercharges and relative to the motion of the center ion at the coordinate origin; this point should be remembered to avoid possible confusion about the motions of ions in the ion atmosphere under the external electric field. In the same section, we also calculate the nonequilibrium component of pressure which is consistent with the velocity—the solution of the NS equation—and depends on the field strength. In this section, we also present some numerical examples for the axial velocity profiles that qualitatively display how ions move under the external electric field. It reveals an interesting aspect of ionic flow in ion atmosphere subjected to an electric field. More detailed numerical analysis of the velocity profiles and their applications will be made in the sequels where the theory of conductance, transport as well as thermodynamic properties, and comparison of the theoretical result with experiment will be discussed. In Sec. V, we examine how one might recover the electrophoretic effect of the Onsager–Wilson theory from the result of the present work. Sec. VI is for discussion and concluding remarks.

II. Pair Correlation Functions and Potentials

The fluid system of interest here is a binary strong electrolyte solution subjected to an external electric field. In the OF theory of transport in electrolyte solutions the evolution equations for ionic pair distribution functions are assumed to obey the OF equations, which are essentially Fokker–Planck type equations^{30,31} in external fields of body force. These equations are coupled to

the Poisson equations for potentials of interaction between ions. This coupled set of second-order differential equations in fact provides an interesting and potentially productive approach to Coulombic interaction systems subject to an external electric field that, in our opinion, has been overlooked in the fields of plasmas and semiconductors.

The OF equations are linear with respect to the potentials because the total force involves the assumption that the total field due to the ions and their atmospheres may be obtained by linear superposition of separate fields. Onsager and Wilson^{21,26} solved the coupled OF and Poisson equations by means of Fourier transforms in a cylindrical coordinate system in which the electric field is aligned to the axis of the cylinder. It should be emphasized that linearizing OF equations with regard to the force does not imply at all that the solutions of the coupled set of equations are linear with respect to the field strength. The assumption only ensures superposition of fields. In any case, it is the point of the Onsager–Wilson theory as far as the OF equations for the ion pair distribution functions are concerned. The formal solutions obtained are formally exact. They can be employed to obtain the formal solution of the hydrodynamic equations for the velocity of the medium. However, the formal results are impractical to use for studying transport properties in electrolyte solutions, unless they are further evaluated more explicitly.

Before presenting the solutions it is useful to note the symmetry properties of the distribution functions and potentials, which are made use of to construct the solutions. The indices j and i will be designated to stand for the positive and negative ion, respectively. We denote by \mathbf{r} the relative distance vector $\mathbf{r} = \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j = -\mathbf{r}_{ji}$ between ions. The ion pair distribution functions are then denoted by $f_{ji}(\mathbf{r}_j, \mathbf{r}_{ij})$ and $f_{ij}(\mathbf{r}_i, \mathbf{r}_{ji})$, where \mathbf{r}_k ($k = i, j$) is the position vector of ion k . This implies that for the nonuniform nonequilibrium system of

interest the distribution functions are spatially nonuniform with respect to the position of ions, e.g., \mathbf{r}_k in the case of $f_{ki}(\mathbf{r}_k, \mathbf{r}_{ik})$. The potentials $\psi_j(\mathbf{r}_j, \mathbf{r}_{ij})$ and $\psi_i(\mathbf{r}_i, \mathbf{r}_{ji})$ obeying the Poisson equations also depend on the position \mathbf{r}_k of the ion k and the relative distance vector $\mathbf{r}_{ji} = -\mathbf{r}_{ij}$ between ions j and i . Henceforth the position vector \mathbf{r}_k will be suppressed in the distribution functions and potentials for the sake of notational brevity. The Fourier transforms of solutions^{18,21,26} for the OF equations and Poisson equations are as follows: the distribution functions are given by

$$f_{ii}(\mathbf{r}) = n^2 + \frac{2ze^2n^2}{\pi Dk_B T} \int_0^\infty d\alpha \cos(\alpha x) \times \left[\frac{(1+R)}{2R^2} K_0(\lambda_1 \rho) + \frac{(1-R)}{2R^2} K_0(\lambda_2 \rho) - \frac{1-R^2}{R^2} K_0(\lambda_3 \rho) \right], \quad (5)$$

$$f_{jj}(\mathbf{r}) = n^2 - \frac{2ze^2n^2}{\pi Dk_B T} \int_0^\infty d\alpha \cos(\alpha x) \times \left[\frac{(1+R)}{2R^2} K_0(\lambda_1 \rho) + \frac{(1-R)}{2R^2} K_0(\lambda_2 \rho) + \frac{1-R^2}{R^2} K_0(\lambda_3 \rho) \right], \quad (6)$$

$$\begin{aligned} f_{ij} &= f_{ji}(\pm \mathbf{r}) \\ &= n^2 + \frac{2n^2 \eta' e}{\pi D} \int_0^\infty d\alpha \cos(\alpha x) \left[\frac{(1+R)}{2R^2} K_0(\lambda_1 \rho) - \frac{(1-R)}{2R^2} K_0(\lambda_2 \rho) \right] \\ &\quad \pm \frac{2n^2 \eta' e \mu'}{\pi D \kappa^2} \int_0^\infty d\alpha \sin(\alpha x) \alpha \times \\ &\quad \left[\frac{(1+R)}{R^2} K_0(\lambda_1 \rho) + \frac{(1-R)}{R^2} K_0(\lambda_2 \rho) - \frac{2}{R^2} K_0(\lambda_3 \rho) \right]. \end{aligned} \quad (7)$$

Here $f_{ii}(\mathbf{r})$ and $f_{jj}(\mathbf{r})$ are the pair distribution functions of two identical ions of species i and j respectively, and $f_{ij}(\mp \mathbf{r})$ and $f_{ji}(\pm \mathbf{r})$ are the pair distribution functions of two different ion species j and i at relative distance $\mathbf{r}_i - \mathbf{r}_j$ and $\mathbf{r}_j - \mathbf{r}_i$, respectively. On the other hand, the potentials of interaction—in fact,

the nonequilibrium parts thereof—are given by

$$\begin{aligned}
\psi_j(\pm \mathbf{r}) &= -\psi_i(\mp \mathbf{r}) \\
&= \frac{2ze}{\pi D} \int_0^\infty d\alpha \cos(\alpha x) \times \\
&\quad \frac{1}{2R^2} [(1+R)K_0(\lambda_1\rho) + (1-R)K_0(\lambda_2\rho) - 2(1-R^2)K_0(\lambda_3\rho)] \\
&\quad \pm \frac{2ze\mu'}{\pi D\kappa^2} \int_0^\infty d\alpha \sin(\alpha x) \frac{\alpha}{R^2} [K_0(\lambda_1\rho) + K_0(\lambda_2\rho) - 2K_0(\lambda_3\rho)].
\end{aligned} \tag{8}$$

The potentials $\psi_j(\pm \mathbf{r})$ and $\psi_i(\mp \mathbf{r})$ are the nonequilibrium potentials beyond the equilibrium potentials, which are the Debye–Hückel potentials.²⁵

In the expressions in Eqs. (5)–(8), x and ρ are, respectively, the axial and radial coordinates of the cylindrical coordinate system; α is the Fourier transform variable; $K_0(\lambda_l\rho)$ is the Bessel function of second kind²⁸ with λ_l defined as follows:

$$\begin{aligned}
\lambda_1^2 &= \alpha^2 + \frac{1}{2}\kappa^2(1+R), \\
\lambda_2^2 &= \alpha^2 + \frac{1}{2}\kappa^2(1-R), \\
\lambda_3^2 &= \alpha^2 + \frac{1}{2}\kappa^2.
\end{aligned} \tag{9}$$

Here R denotes

$$R = \sqrt{1 - \frac{4\mu'^2\alpha^2}{\kappa^4}}. \tag{10}$$

Furthermore, since the external field is assumed to be directed in the positive x direction, the functions in the present theory is axially symmetric around the x axis, and hence do not depend on the azimuthal angle θ of the cylindrical coordinates. For the binary electrolyte under consideration, if z_j and z_i are charge numbers, then $z = |z_j| = |z_i|$; e is the unit charge; D is the dielectric constant of the medium; μ' and η' are defined by

$$\mu' = \frac{zeX}{k_B T}, \quad \eta' = \frac{ze}{k_B T} \tag{11}$$

with X denoting the field strength, k_B the Boltzmann constant, T the absolute temperature; κ is the Debye parameter of the electrolyte solution

$$\kappa = \sqrt{\frac{4\pi e^2 n}{Dk_B T} \sum_k z_k^2 c_k} \quad \left(c_k = \frac{n_k}{n} \right), \quad (12)$$

where n is the density and n_k the density of k . For a symmetric binary electrolyte κ is given by

$$\kappa = \sqrt{\frac{4\pi z^2 e^2 n}{Dk_B T}} \quad (z = |z_1| = |z_2|)$$

The important feature about the ion pair distribution functions and potentials presented above is their symmetry properties with respect to interchange of the ion positions:

$$f_{ii}(\mathbf{r}) = f_{ii}(-\mathbf{r}), \quad f_{jj}(\mathbf{r}) = f_{jj}(-\mathbf{r}), \quad f_{ji}(\pm\mathbf{r}) = f_{ij}(\mp\mathbf{r}) \quad (13)$$

and

$$\psi_j(\pm\mathbf{r}) = -\psi_i(\mp\mathbf{r}), \quad (14)$$

and the sign ambiguity in Eqs. (7) and (8) refers to the ion involved, namely, positive or negative ion. It should be remembered that the ion positions are suppressed in the distribution functions and potentials; for example, $f_{ji}(\pm\mathbf{r}) \equiv f_{ji}(\mathbf{r}_j, \mathbf{r}_{ij})$ and $\psi_j(\pm\mathbf{r}) \equiv \psi_j(\mathbf{r}_j, \pm\mathbf{r}_{ij})$ with $\mathbf{r} = \mathbf{r}_{ij}$. It should be reiterated that the functions in Eqs. (5)–(8) do not depend on the angle variable θ owing to the cylindrical symmetry of the system under consideration. For the derivations of symmetry properties of the ion pair distribution functions and potentials of interaction the reader is referred to Refs. 18, 21, and 26. Here we simply note that the symmetry properties of Eq. (13) and Eq. (14) are for interchange of ionic positions or indices for ions. Although they are not necessary for solving the hydrodynamic equations, the Fourier transforms given in Eqs. (5)–(8) are explicitly evaluated by using the same method for the velocity and pressure in Appendix A for completeness.

The Fourier transforms on the right hand sides of Eqs. (5)–(8) represent nonequilibrium field-dependent parts of distribution functions and potentials. Especially, Eq. (8) must be combined with the Debye potential if one wishes to calculate the full potential function of ion j .

III. Hydrodynamic Equation and Its Solution

It is well known that ions interacting through long range Coulomb potentials produce their ion atmospheres of the mean radius given by the Debye length κ^{-1} centered around each of them. In an external electric field the ion atmospheres of ions interact with the field producing “dressed” local field which in turn influences the hydrodynamic flow and movements of ions in the solution. Such a dressed body-force is an input when the hydrodynamics of an electrolyte solution is sought, subject to suitable boundary conditions. Such a force must be calculated to initiate the solution of hydrodynamic equations—namely, the NS equation in the present case. It can be calculated by using the potential functions given in Eq. (8). In this study we limit the investigation to the case of laminar flow, which allows neglecting the nonlinear inertial term in the hydrodynamic equation. We assume that there are no body-forces other than an electric field applied.

A. Local Electric Field

Assume the field is aligned along the x axis. Since the charge density is given by the Poisson equation, and the force due to the field on charge density ρ by

$$F_x = \rho X = -\frac{DX}{4\pi} \nabla^2 \psi(\mathbf{r}), \quad (15)$$

on substituting the potential function given in the previous section [see Eq. (8)], we find the local force in the form

$$\begin{aligned}
F_x = & -\frac{zeX}{2\pi^2} \int_0^\infty d\alpha \frac{1}{2R^2} \{ (1+R) \nabla^2 [\cos(\alpha x) K_0(\lambda_1 \rho)] \\
& + (1-R) \nabla^2 [\cos(\alpha x) K_0(\lambda_2 \rho)] - 2(1-R^2) \nabla^2 [\cos(\alpha x) K_0(\lambda_3 \rho)] \} \\
& - \frac{zeX\mu'}{2\pi^2\kappa^2} \int_0^\infty d\alpha \frac{\alpha}{R^2} \{ \nabla^2 [\sin(\alpha x) K_0(\lambda_1 \rho)] + \nabla^2 [\sin(\alpha x) K_0(\lambda_2 \rho)] \\
& - 2\nabla^2 [\sin(\alpha x) K_0(\lambda_3 \rho)] \}.
\end{aligned} \tag{16}$$

For a binary electrolyte solution this is in fact the total local force density. It is a “dressed” force if we may adopt a modern terminology often used in many-body physics. Since the Laplacian operator in the cylindrical coordinates (x, ρ, θ) chosen is given by

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \theta^2} \tag{17}$$

and the gradient operator by

$$\nabla = \boldsymbol{\delta}_\rho \frac{\partial}{\partial \rho} + \boldsymbol{\delta}_\theta \frac{1}{\rho} \frac{\partial}{\partial \theta} + \boldsymbol{\delta}_x \frac{\partial}{\partial x}, \tag{18}$$

where $\boldsymbol{\delta}_x$, $\boldsymbol{\delta}_\rho$, and $\boldsymbol{\delta}_\theta$ are unit vectors in the cylindrical coordinate system, it follows that

$$\nabla^2 \begin{pmatrix} \cos(\alpha x) \\ \sin(\alpha x) \end{pmatrix} K_0(\lambda_l \rho) = \begin{pmatrix} \cos(\alpha x) \\ \sin(\alpha x) \end{pmatrix} \left(\frac{1}{\rho} \frac{d}{d\rho} \rho \frac{d}{d\rho} - \alpha^2 \right) K_0(\lambda_l \rho). \tag{19}$$

However, because the Bessel function $K_0(\lambda_l \rho)$ obeys the differential equation²⁸

$$\left(\frac{1}{\rho} \frac{d}{d\rho} \rho \frac{d}{d\rho} - \lambda_l^2 \right) K_0(\lambda_l \rho) = 0, \tag{20}$$

we obtain

$$\nabla^2 \begin{pmatrix} \cos(\alpha x) \\ \sin(\alpha x) \end{pmatrix} K_0(\lambda_l \rho) = (\lambda_l^2 - \alpha^2) \begin{pmatrix} \cos(\alpha x) \\ \sin(\alpha x) \end{pmatrix} K_0(\lambda_l \rho) \tag{21}$$

for $l = 1, 2, 3$. Therefore the local external force is given by

$$F_x = \overline{C}_l \cos(\alpha x) K_0(\lambda_l \rho) + \overline{S}_l \sin(\alpha x) K_0(\lambda_l \rho), \tag{22}$$

where the repeated index implies a sum over the index (Einstein convention) and symbols $\overline{\mathcal{C}}_l$ and $\overline{\mathcal{S}}_l$ are the abbreviations for the following:

$$\overline{\mathcal{C}}_l = -\frac{zeX}{2\pi^2} \int_0^\infty d\alpha \begin{cases} \frac{(1+R)}{2R^2} (\lambda_1^2 - \alpha^2) & \text{for } K_0(\lambda_1\rho) \\ \frac{(1-R)}{2R^2} (\lambda_2^2 - \alpha^2) & \text{for } K_0(\lambda_2\rho) \\ -\frac{(1-R^2)}{R^2} (\lambda_3^2 - \alpha^2) & \text{for } K_0(\lambda_3\rho) \end{cases} \quad (23)$$

and

$$\overline{\mathcal{S}}_k = -\frac{zeX}{2\pi^2} \frac{\mu'}{\kappa^2} \int_0^\infty d\alpha \begin{cases} \frac{\alpha}{R^2} (\lambda_1^2 - \alpha^2) & \text{for } K_0(\lambda_1\rho) \\ \frac{\alpha}{R^2} (\lambda_2^2 - \alpha^2) & \text{for } K_0(\lambda_2\rho) \\ -\frac{2\alpha}{R^2} (\lambda_3^2 - \alpha^2) & \text{for } K_0(\lambda_3\rho) \end{cases} . \quad (24)$$

The force F_x is an input for the NS equation of interest. The external force zeX therefore is dressed up by the extent of the integral factors in Eqs. (23) and (24) arising from the Brownian motion of ions interacting with the external field and among themselves through Coulomb potentials and consequently depending on the field and density.

B. Navier–Stokes Equation

For a steady flow the Navier–Stokes equation takes the form

$$\rho \mathbf{v} \cdot \nabla \mathbf{v} - \eta_0 \nabla^2 \mathbf{v} - \eta_b \nabla (\nabla \cdot \mathbf{v}) = -\nabla p + \mathbf{F}, \quad (25)$$

where ρ is the density, η_0 is the shear viscosity, η_b is the bulk viscosity, p is the pressure, and \mathbf{F} is the body (external) force density. For an incompressible fluid $\nabla \cdot \mathbf{v} = 0$ and for a fluid undergoing laminar flow of low Reynolds number (typically $\text{Re} = O(10^{-6})$ at the field gradient of 1 kV/m in aqueous solution) the inertial term can be neglected. Thus the Navier–Stokes equations for velocity \mathbf{v} are given by the pair of equations

$$-\eta_0 \nabla^2 \mathbf{v} = -\nabla p + \mathbf{F}, \quad (26)$$

$$\nabla \cdot \mathbf{v} = 0. \quad (27)$$

This set is called the Stokes equation by some authors, but we will refer to it simply as the NS equation for an incompressible fluid in this work. Note that

the presence of an external field makes the pressure nonuniform in space. It is interesting to note that if *curl* of Eq. (42) is taken, the ∇p term vanishes and Eq. (26) takes the form

$$\eta_0 \nabla \times \nabla \times \nabla \times \mathbf{v} = \nabla \times \mathbf{F}. \quad (28)$$

Since $\nabla \times \nabla \times \mathbf{v} = \nabla (\nabla \cdot \mathbf{v}) - \nabla^2 \mathbf{v}$ by vector algebra, the two equations (26) and (27) may be combined into a single equation

$$\eta_0 \nabla \times \nabla \times \mathbf{v} = -\nabla p + \mathbf{F}. \quad (29)$$

This is equivalent to the Stokes equation, (26) and (27) for an incompressible fluid. For the present problem $\mathbf{F} = \delta_x F_x$, where δ_x is the unit vector along the x axis.

To solve Eq. (29) for \mathbf{v} , we observe $\nabla \cdot \mathbf{v} = 0$, which means that there exists an axial vector \mathbf{A} such that $\mathbf{v} = \nabla \times \mathbf{A}$, where \mathbf{A} must depend on position vector \mathbf{r} and field vector \mathbf{X} , both of which are ordinary vectors, that is, polar vectors. Therefore \mathbf{A} must be a vector function that must also be an axial vector, because \mathbf{v} is a polar vector. These two conditions are met simultaneously if $\mathbf{A} = \nabla \times \mathbf{a}$, where $\mathbf{a} = \mathbf{a}(\mathbf{r}, \mathbf{X})$ is a polar vector. Note in this regard that the *curl* of an axial vector is a polar vector, and the *curl* of a polar vector is an axial vector. Thus we may write \mathbf{v} in a general form

$$\mathbf{v} = \nabla \times \nabla \times \mathbf{a} + \mathbf{v}^0, \quad (30)$$

where \mathbf{v}^0 is a constant satisfying the appropriate boundary conditions of the velocity. Note that here \mathbf{a} is a polar vector. Since $\mathbf{a} \rightarrow 0$ and also \mathbf{v} should vanish as $|\mathbf{r}| \rightarrow \infty$, it follows $\mathbf{v}^0 = 0$. Thus we will set $\mathbf{v}^0 = 0$ henceforth.

As the first step to formally solve Eq. (29), substitute Eq. (30) with $\mathbf{v}^0 = 0$ into Eq. (29) to obtain the equation

$$\eta_0 \nabla \times \nabla \times \nabla \times \nabla \times \mathbf{a} = -\nabla p + \mathbf{F}. \quad (31)$$

To simplify the quadruple *curl* term on the left hand side we observe that by vector algebra

$$\nabla \times \nabla \times \mathbf{a} = \nabla (\operatorname{div} \mathbf{a}) - \nabla^2 \mathbf{a}, \quad (32)$$

$$\nabla \times \nabla \times \nabla (\nabla \cdot \mathbf{a}) = 0. \quad (33)$$

Then take *curl* \times *curl* of Eq. (32) to obtain

$$\nabla \times \nabla \times (\nabla^2 \mathbf{a}) = \nabla (\nabla^2 \operatorname{div} \mathbf{a}) - \nabla^2 (\nabla^2 \mathbf{a}). \quad (34)$$

It then follows that

$$\begin{aligned} \nabla \times \nabla \times \nabla \times \nabla \times \mathbf{a} &= \nabla \times \nabla \times \nabla (\nabla \cdot \mathbf{a}) - \nabla \times \nabla \times (\nabla^2 \mathbf{a}) \\ &= -\nabla \times \nabla \times (\nabla^2 \mathbf{a}). \end{aligned} \quad (35)$$

Upon using Eq. (32) in Eq. (35) and substituting the result into Eq. (31), we obtain the equation

$$\eta_0 \nabla^2 \nabla^2 \mathbf{a} - \mathbf{F} = \nabla (\eta_0 \nabla^2 \operatorname{div} \mathbf{a} - p), \quad (36)$$

which is equivalent to Eq. (29) or the NS equation. Because the left and right of Eq. (36) are of two different kinds of vectors, the equation is satisfied if

$$\eta_0 \nabla^2 \nabla^2 \mathbf{a} = \mathbf{F}, \quad (37)$$

$$p = p_0 + \eta_0 \nabla^2 \operatorname{div} \mathbf{a}.$$

In this manner, we have deduced the equation to determine the vector \mathbf{a} , namely, Eq. (37), given the force vector \mathbf{F} , Eq. (22) in the previous subsection. Thus we have obtained the formal solutions for \mathbf{v} and p satisfying the NS equation, Eq. (29), in terms of vector \mathbf{a} . The solution of the NS equation is now reduced to that of Eq. (37), a fourth-order differential equation, given \mathbf{F} that is provided by the OF equations and the Poisson equations. In summary of these results,

we have

$$\mathbf{v} = \nabla \times \nabla \times \mathbf{a} + \mathbf{v}^0 = \nabla \times \nabla \times \mathbf{a}, \quad (38)$$

$$p = p_0 + \eta_0 \nabla^2 (\nabla \cdot \mathbf{a}). \quad (39)$$

Vector \mathbf{a} is determined by solving Eq. (37) in terms of the local force density given by Eq. (22).

Eq. (38) differs from Wilson's expression for \mathbf{v} in two aspects: a negative sign appears in his equation, probably a typo; and the absence of constant term \mathbf{v}_0 , which turns out equal to zero. It turns out that the sign error in the $\text{curl} \times \text{curl}$ term on the right of Eq. (38) was later compensated by another sign error in the process of determining vector \mathbf{a} described in the following.

In Eq. (39) p_0 is a homogeneous pressure uniform in space, that is, the equilibrium pressure. This equilibrium pressure must be either supplied phenomenologically by using thermodynamics or from the statistical mechanics of the electrolyte solution.^{32,33} For example, it may be calculated from the formula

$$p_0 = nk_B T - \frac{2\pi}{3} \sum_{i < j} n_i n_j \int_0^\infty dr r^3 \frac{du_{ij}}{dr} g_{ij}^0(r), \quad (40)$$

where u_{ij} is the intermolecular potential of pair (i, j) and $g_{ij}^0(r)$ is the equilibrium pair correlation function. The index i runs over the species in the fluid, including ions. Determination of $g_{ij}^0(r)$ should be made by following the modern theory of equilibrium Coulomb (ionic) fluids.^{32,33} This homogeneous solution for p is also absent in Wilson's result for p .

To solve Eq. (37), substitute Eq. (22) into the former, which then reads

$$\nabla^2 (\nabla^2 \mathbf{a}) = \boldsymbol{\delta}_x C_l \cos(\alpha x) K_0(\lambda_l \rho) + \boldsymbol{\delta}_x S_l \sin(\alpha x) K_0(\lambda_l \rho), \quad (41)$$

where

$$C_l = \frac{\overline{C}_l}{\eta_0}, \quad S_l = \frac{\overline{S}_l}{\eta_0}. \quad (42)$$

Recalling Eq. (21), we find

$$\nabla^2 \mathbf{a} = \delta_x C_l \frac{\cos(\alpha x) K_0(\lambda_l \rho)}{\lambda_l^2 - \alpha^2} + \delta_x S_l \frac{\sin(\alpha x) K_0(\lambda_l \rho)}{\lambda_l^2 - \alpha^2} + \delta_x A^*, \quad (43)$$

where A^* is the homogeneous solution obeying the equation

$$\nabla^2 (\nabla^2 \mathbf{A}^*) = 0 \quad (44)$$

with $\mathbf{A}^* = \delta_x A^*$. The solution \mathbf{A}^* must fit the boundary conditions at ρ infinite.

Thus we choose

$$\mathbf{A}^* = -\delta_x C_l \frac{\cos(\alpha x) K_0(\alpha \rho)}{\lambda_l^2 - \alpha^2} - \delta_x S_l \frac{\sin(\alpha x) K_0(\alpha \rho)}{\lambda_l^2 - \alpha^2}. \quad (45)$$

Therefore we obtain the equation

$$\nabla^2 \mathbf{a} = \delta_x C_l \frac{\cos(\alpha x) [K_0(\lambda_l \rho) - K_0(\alpha \rho)]}{\lambda_l^2 - \alpha^2} + \delta_x S_l \frac{\sin(\alpha x) [K_0(\lambda_l \rho) - K_0(\alpha \rho)]}{\lambda_l^2 - \alpha^2}. \quad (46)$$

The solution of this inhomogeneous second-order differential equation is sought in the form

$$\mathbf{a} = \delta_x \left[C_l \frac{\cos(\alpha x)}{\lambda_l^2 - \alpha^2} + S_l \frac{\sin(\alpha x)}{\lambda_l^2 - \alpha^2} \right] \times \{b_1 [K_0(\lambda_l \rho) - K_0(\alpha \rho)] + b_2 [K_0(\beta_l \rho) - K_0(\alpha \rho)]\}, \quad (47)$$

where b_1 , b_2 , and β_l are constants determined as follows—note that in Wilson's dissertation only the final results for the coefficients are given. On inserting this into Eq. (46) we find

$$b_1 (\lambda_l^2 - \alpha^2) K_0(\lambda_l \rho) + b_2 (\beta_l^2 - \alpha^2) K_0(\beta_l \rho) = K_0(\lambda_l \rho) - K_0(\alpha \rho)$$

or

$$[b_1 (\lambda_l^2 - \alpha^2) - 1] K_0(\lambda_l \rho) + b_2 (\beta_l^2 - \alpha^2) K_0(\beta_l \rho) + K_0(\alpha \rho) = 0. \quad (48)$$

Since $K_0(\lambda_l \rho)$, $K_0(\beta_l \rho)$, and $K_0(\alpha \rho)$ are not equal to zero for all values of ρ , if b_1 and b_2 are chosen such that

$$b_1 = \frac{1}{\lambda_l^2 - \alpha^2} \quad (49)$$

and

$$\lim_{\beta_l \rightarrow \alpha} b_2 (\beta_l^2 - \alpha^2) K_0(\beta_l \rho) = -K_0(\alpha \rho), \quad (50)$$

then Eq. (47) is a solution of Eq. (46). Eq. (50) implies

$$b_2 = -\frac{1}{(\beta_l^2 - \alpha^2)}. \quad (51)$$

Finally, we obtain for the solution of Eq. (46)

$$\mathbf{a} = \boldsymbol{\delta}_x [C_i \cos(\alpha x) + S_i \sin(\alpha x)] \times \left\{ \frac{1}{(\lambda_i^2 - \alpha^2)^2} [K_0(\lambda_i \rho) - K_0(\alpha \rho)] + \frac{1}{(\lambda_i^2 - \alpha^2) \alpha^2} \frac{\alpha \rho}{2} K_1(\alpha \rho) \right\}. \quad (52)$$

Here again, there is a sign difference between the last term on the right of Eq. (52) and the corresponding term in Wilson's equation, Eq. (4.11), in his dissertation.²¹ This particular term gives rise to the aforementioned divergence-causing integral, but since it is essentially ignored in his work this sign error would not affect his final result for the electrophoretic effect.

Since the vector \mathbf{a} is now obtained, it is possible to calculate the velocity—namely, the solution of the NS equation—and pressure by using Eqs. (38) and (39), respectively. For the purpose we calculate $\text{div } \mathbf{a}$, $\nabla_x \text{div } \mathbf{a}$, and $\nabla_\rho \text{div } \mathbf{a}$. Since for the present problem

$$\text{div } \mathbf{a} = \frac{\partial a_x}{\partial x} \quad (53)$$

owing to the fact that $\mathbf{F} = \boldsymbol{\delta}_x F_x$ and hence $a_\rho = a_\theta = 0$ identically, we find

$$\text{div } \mathbf{a} = -[C_l \sin(\alpha x) - S_l \cos(\alpha x)] \times \left\{ \frac{\alpha}{(\lambda_l^2 - \alpha^2)^2} [K_0(\lambda_l \rho) - K_0(\alpha \rho)] + \frac{\rho}{2(\lambda_l^2 - \alpha^2)} K_1(\alpha \rho) \right\}. \quad (54)$$

From this follow the expressions

$$\nabla_x \text{div } \mathbf{a} = -[C_l \cos(\alpha x) + S_l \sin(\alpha x)] \times \left\{ \frac{\alpha^2}{(\lambda_l^2 - \alpha^2)^2} [K_0(\lambda_l \rho) - K_0(\alpha \rho)] + \frac{\alpha \rho}{2(\lambda_l^2 - \alpha^2)} K_1(\alpha \rho) \right\}, \quad (55)$$

$$\nabla_\rho \operatorname{div} \mathbf{a} = [C_l \sin(\alpha x) - S_l \cos(\alpha x)] \alpha \times \left\{ \frac{\lambda_l K_1(\lambda_l \rho)}{(\lambda_l^2 - \alpha^2)^2} - \frac{\alpha K_1(\alpha \rho)}{(\lambda_l^2 - \alpha^2)^2} + \frac{\rho}{2(\lambda_l^2 - \alpha^2)} K_0(\alpha \rho) \right\}, \quad (56)$$

$$\nabla^2 \left(\frac{\partial a_x}{\partial x} \right) = -\nabla^2 [C_l \sin(\alpha x) - S_l \cos(\alpha x)] \left\{ \frac{\alpha K_0(\lambda_l \rho)}{(\lambda_l^2 - \alpha^2)} - 2\alpha K_0(\alpha \rho) \right\}, \quad (57)$$

for which we have used the recurrence relation for the Bessel functions^{28,34}

$$\begin{aligned} K'_0(z) &= -K_1(z), \\ K'_1(z) &= -K_0(z) - \frac{1}{z} K_1(z). \end{aligned} \quad (58)$$

Here the prime denotes the derivative with respect to z .

C. Formal Solution for the Axial Velocity

It is now possible to calculate the formal solution for the axial component of the velocity. Since

$$(\nabla \times \nabla \times \mathbf{a})_x = \nabla_x (\operatorname{div} \mathbf{a}) - \nabla^2 a_x,$$

by using the formulas for $\nabla_x (\operatorname{div} \mathbf{a})$ and $\nabla^2 a_x$ we obtain the formal solution for the axial velocity component for all values of x and ρ :

$$\begin{aligned} \mathbf{v}_x(x, \rho, 0) &= -C_l \cos(\alpha x) \times \\ &\quad \left\{ \frac{\lambda_l^2}{(\lambda_l^2 - \alpha^2)^2} [K_0(\lambda_l \rho) - K_0(\alpha \rho)] + \frac{\alpha \rho}{2(\lambda_l^2 - \alpha^2)} K_1(\alpha \rho) \right\} \\ &\quad - S_l \sin(\alpha x) \times \\ &\quad \left\{ \frac{\lambda_l^2}{(\lambda_l^2 - \alpha^2)^2} [K_0(\lambda_l \rho) - K_0(\alpha \rho)] + \frac{\alpha \rho}{2(\lambda_l^2 - \alpha^2)} K_1(\alpha \rho) \right\}. \end{aligned} \quad (59)$$

This formula does not agree with Wilson's Eq. (4.17): $K_0(\alpha \rho)$ is missing in his second term, probably another typo; and the last term is $K_0(\alpha \rho)$ instead of $K_1(\alpha \rho)$ as it is here. Since he does not list the sine transform term (the second group of the terms in Eq. (59)) it is not possible to compare the present formula with his formula for the sine transform part.

On substitution of C_l and S_l the axial velocity formula can be further simplified to the form

$$\mathbf{v}_x(x, \rho, 0) = \frac{zeX}{2\pi^2\eta_0} I_c(x, \rho, 0) + \frac{zeX}{2\pi^2\eta_0} \left(\frac{\mu'}{\kappa^2} \right) I_s(x, \rho, 0), \quad (60)$$

where

$$\begin{aligned} I_c(x, \rho, 0) = \int_0^\infty d\alpha \cos(\alpha x) \times \\ \left\{ \frac{1}{\kappa^2 R^2} [\lambda_1^2 K_0(\lambda_1 \rho) + \lambda_2^2 K_0(\lambda_2 \rho) - 2\lambda_3^2 (1 - R^2) K_0(\lambda_3 \rho)] \right. \\ \left. - \frac{2\lambda_3^2}{\kappa^2} K_0(\alpha \rho) + \frac{\alpha \rho}{2} K_1(\alpha \rho) \right\} \end{aligned} \quad (61)$$

and

$$\begin{aligned} I_s(x, \rho, 0) = \int_0^\infty d\alpha \sin(\alpha x) \left\{ \frac{2\alpha}{\kappa^2 R^2} \left[\frac{\lambda_1^2}{(1 + R)} K_0(\lambda_1 \rho) + \frac{\lambda_2^2}{(1 - R)} K_0(\lambda_2 \rho) \right. \right. \\ \left. \left. - 2\lambda_3^2 K_0(\lambda_3 \rho) \right] - \frac{4\alpha^3}{\kappa^2 (1 - R^2)} K_0(\alpha \rho) \right\}. \end{aligned} \quad (62)$$

Wilson²¹ evaluated the integrals in $I_c(x, \rho, 0)$ at $x = \rho = 0$ at which point $I_s(x, \rho, 0)$ is identically equal to zero owing to the $\sin(\alpha x)$ factor. But the last integrand in $I_c(x, \rho, 0)$ then gives rise to $\frac{1}{2}$, which yields a divergent result

$$\int_0^\infty \frac{1}{2} d\alpha = \infty. \quad (63)$$

Wilson argued that this term does not contribute to the electrophoretic effect because its contour integral along a semicircle in the complex plane vanishes. However, this argument is fallacious because the integrand of this integral does not satisfy the Jordan lemma²⁹ for the contour integral involving a contour along an infinite semicircle. Moreover, even if the contour integral along the infinite semicircle vanishes, it does not necessarily mean the integral $\int_0^\infty \frac{1}{2} d\alpha$ vanishes. This, on the contrary, is manifestly divergent and does not need a method of contour integration for evaluation.

To avoid this difficulty we will evaluate the integrals in I_c and I_s for arbitrary values of x and ρ . We will then apply the results to the calculation of

electrophoretic effect in the sequel; as a matter of fact, we will have to explore a way to obtain it in a finite form.

This evaluation of $\mathbf{v}_x(x, \rho, 0)$ together with evaluations of the transversal velocity and pressure for arbitrary values of x and ρ constitutes the principal contribution of this work to the hydrodynamics of strong binary electrolyte solutions in an external electric field. The results are the complete solution of the NS equation for binary electrolyte solutions in an external electric field; they are not only new, but also portend the necessity of a revision of Wilson's result for the ionic conductivity.^{18,21}

D. Formal Solution for the Transversal Velocity

By using the relation

$$(\nabla \times \nabla \times \mathbf{a})_\rho = \nabla_\rho (\text{div } \mathbf{a}) - \nabla^2 \mathbf{a}_\rho = \nabla_\rho (\text{div } \mathbf{a}) \quad (64)$$

in the case of $a_\rho = a_\theta = 0$ we find the transversal velocity component in the form

$$\mathbf{v}_\rho(x, \rho, 0) = \frac{zeX}{2\pi^2\eta_0} \frac{\mu'}{\kappa^2} J_c(x, \rho, 0) - \frac{zeX}{2\pi^2\eta_0} J_s(x, \rho, 0), \quad (65)$$

where

$$J_c(x, \rho, 0) = \int_0^\infty d\alpha \cos(\alpha x) \left\{ \frac{\alpha^2}{\kappa^2 R^2 (1 - R^2)} [\lambda_1 (1 - R) K_1(\lambda_1 \rho) + \lambda_2 (1 + R) K_1(\lambda_2 \rho) - 2\lambda_3 (1 - R^2) K_1(\lambda_3 \rho)] - \frac{4\alpha^3}{\kappa^2 (1 - R^2)} K_1(\alpha \rho) \right\}, \quad (66)$$

$$J_s(x, \rho, 0) = \int_0^\infty d\alpha \sin(\alpha x) \left\{ \frac{\alpha}{\kappa^2 R^2} [\lambda_1 K_1(\lambda_1 \rho) + \lambda_2 K_1(\lambda_2 \rho) - 2\lambda_3 (1 - R^2) K_1(\lambda_3 \rho)] - \frac{2\alpha^2}{\kappa^2} K_1(\alpha \rho) + \frac{\alpha \rho}{2} K_0(\alpha \rho) \right\}. \quad (67)$$

The integrals in these expressions can be evaluated for all values of x and ρ in a similar manner to the axial velocity, as will be shown.

E. Formal Solution for Pressure

Since for the present system the (nonequilibrium) pressure is given by

$$p = p_0 + \eta_0 \nabla^2 \left(\frac{\partial a_x}{\partial x} \right),$$

it is easy to calculate it from Eq. (57):

$$\begin{aligned} p - p_0 = & \frac{zeX}{2\pi^2} \int_0^\infty d\alpha \frac{\alpha \sin(\alpha x)}{2R^2} [(1+R) K_0(\lambda_1 \rho) \\ & + (1-R) K_0(\lambda_2 \rho) - 2(1-R^2) K_0(\lambda_3 \rho)] \\ & - \frac{zeX}{2\pi^2} \int_0^\infty d\alpha \alpha \sin(\alpha x) K_0(\alpha \rho) \\ & - \frac{zeX\mu'}{2\pi^2 \kappa^2} \int_0^\infty d\alpha \frac{\alpha^2 \cos(\alpha x)}{R^2} [K_0(\lambda_1 \rho) + K_0(\lambda_2 \rho) - 2K_0(\lambda_3 \rho)]. \quad (68) \end{aligned}$$

The formula presented above represents a nonequilibrium part of pressure that is consistent with the velocity components obtained as the solution of the NS equation for a fluid in an external electric field. We have already mentioned on how the equilibrium (homogeneous) pressure might be calculated^{32,33}; see Eq. (40).

IV. Evaluation of the Formal Solutions for Velocities and Pressure

The formal Fourier transform solutions for the axial and transversal velocity components and pressure, though exact, need explicit evaluation as functions of x and ρ before they can be made to readily indicate their profiles in the configuration space $(x, \rho, 0)$ and applied to study transport and nonequilibrium properties of electrolyte solutions. Here we will reduce them to either analytic forms or quadratures which can be readily evaluated by means of simple numerical methods or approximation methods. One can, of course, bypass this procedure and simply resort to a numerical computation method to evaluate the formal Fourier transform solutions, but this would be rather cumbersome

and time consuming computationally, especially because most of the integrands involved are singular at some points on the real axis and one has to make use of the methods for singular integrals³⁵ to evaluate them. The method of evaluation for the integrals discussed below makes it unnecessary to use a direct numerical evaluation method.

It was mentioned earlier that Wilson evaluated the integrals by taking the position variables (x, ρ) at the coordinate origin $(x = 0, \rho = 0)$ and that such a choice of position gives rise to a divergent integral, Eq. (63). In the following we do not assume a particular set of values for x and ρ , but evaluate them either by means of the method of contour integration or by conventional methods of evaluation.

It is convenient for evaluating the integrals to make use of reduced variables. We use the following reduced variables for the purpose:

$$\hat{\mathbf{v}} = \left(2\sqrt{2}\pi^2\eta_0/zeX\kappa \right) \mathbf{v}, \quad (69)$$

$$t = \sqrt{2}\alpha/\kappa, \quad r = \rho\kappa/\sqrt{2}, \quad \bar{x} = x\kappa/\sqrt{2}, \quad \xi = \mu'/\kappa, \quad (70)$$

$$\omega_1 = \frac{\sqrt{2}\lambda_1}{\kappa} = \sqrt{1+t^2 + \sqrt{1-2\xi^2t^2}}, \quad (71)$$

$$\omega_2 = \frac{\sqrt{2}\lambda_2}{\kappa} = \sqrt{1+t^2 - \sqrt{1-2\xi^2t^2}}, \quad (72)$$

$$\omega_3 = \frac{\sqrt{2}\lambda_3}{\kappa} = \sqrt{1+t^2}. \quad (73)$$

We also use the following abbreviations:

$$\bar{\omega}_1 = \sqrt{1-y^2 + \sqrt{1+2\xi^2y^2}}, \quad \bar{\omega}_3 = \sqrt{1-y^2}, \quad \bar{\omega} = \frac{\sqrt{1+2\xi^2}}{\sqrt{2}\xi}. \quad (74)$$

A. Axial Velocity

The reduced axial velocity then takes the form

$$\hat{\mathbf{v}}_x(x, \rho, 0) = \frac{1}{2}K_c + \frac{\xi}{\sqrt{2}}K_s, \quad (75)$$

where

$$K_c(\bar{x}, r, 0) = \int_0^\infty dt \cos(t\bar{x}) \frac{1}{(1 - 2\xi^2 t^2)} \times \\ [\omega_1^2 K_0(\omega_1 r) + \omega_2^2 K_0(\omega_2 r) - 4\xi^2 t^2 \omega_3^2 K_0(\omega_3 r)] \\ + 2 \int_0^\infty dt \cos(t\bar{x}) \left[-\omega_3^2 K_0(rt) + \frac{rt}{2} K_1(rt) \right], \quad (76)$$

$$K_s(\bar{x}, r, 0) = \int_0^\infty dt \frac{t \sin(t\bar{x})}{(1 - 2\xi^2 t^2)} \times \\ \left[\frac{\omega_1^2 K_0(\omega_1 r)}{(1 + R)} + \frac{\omega_2^2 K_0(\omega_2 r)}{(1 - R)} - 2\omega_3^2 K_0(\omega_3 r) \right] \\ - \frac{1}{\xi^2} \int_0^\infty dt t \sin(t\bar{x}) K_0(rt). \quad (77)$$

It is convenient to decompose these integrals into various components for the sake of separate evaluations as below:

$$K_c(\bar{x}, r, 0) = K_1^c + K_2^c - 4\xi^2 K_3^c - 2K_4^c + rK_5^c, \quad (78)$$

$$K_s(\bar{x}, r, 0) = K_1^s + K_2^s - 2K_3^s - \frac{1}{\xi^2} K_4^s, \quad (79)$$

where

$$K_1^c = \int_0^\infty dt \cos(t\bar{x}) \frac{\omega_1^2}{(1 - 2\xi^2 t^2)} K_0(\omega_1 r), \quad (80)$$

$$K_2^c = \int_0^\infty dt \cos(t\bar{x}) \frac{\omega_2^2}{(1 - 2\xi^2 t^2)} K_0(\omega_2 r), \quad (81)$$

$$K_3^c = \int_0^\infty dt \cos(t\bar{x}) \frac{t^2 \omega_3^2}{(1 - 2\xi^2 t^2)} K_0(\omega_3 r), \quad (82)$$

$$K_4^c = \int_0^\infty dt \cos(t\bar{x}) \omega_3^2 K_0(rt), \quad (83)$$

$$K_5^c = \int_0^\infty dt \cos(t\bar{x}) t K_1(rt), \quad (84)$$

and

$$K_1^s = \int_0^\infty dt \sin(t\bar{x}) \frac{t\omega_1^2 K_0(\omega_1 r)}{(1 - 2\xi^2 t^2)(1 + R)}, \quad (85)$$

$$K_2^s = \int_0^\infty dt \sin(t\bar{x}) \frac{t\omega_2^2 K_0(\omega_2 r)}{(1 - 2\xi^2 t^2)(1 - R)}, \quad (86)$$

$$K_3^s = \int_0^\infty dt \sin(t\bar{x}) \frac{t\omega_3^2 K_0(\omega_3 r)}{(1 - 2\xi^2 t^2)}, \quad (87)$$

$$K_4^s = \int_0^\infty dt t \sin(t\bar{x}) K_0(rt). \quad (88)$$

Henceforth, when the reduced set of variables is used, we will omit the overbar from \bar{x} for notational brevity and understand by x the reduced variable \bar{x} as defined earlier; see Eqs. (69)–(72).

1. Integrals Amenable to Conventional Methods of Evaluation

We first treat K_4^c , K_5^c , and K_4^s , which are all amenable to conventional methods of evaluation and give rise to elementary functions of x and ρ .

(a) K_4^c

The integrals listed above can be evaluated by using the integral representation²⁸ of the Bessel function $K_\nu(rt)$ of integer order:

$$K_\nu(z) = \int_0^\infty ds e^{-z \cosh s} \cosh(\nu s) \quad \left(|\arg z| < \frac{\pi}{2} \right). \quad (89)$$

On substitution of this integral representation into integral K_4^c and interchanging the order of integration followed by change of variables we obtain

$$K_4^c = \frac{\pi}{2(x^2 + r^2)^{1/2}} - \frac{\pi(2x^2 - r^2)}{2(r^2 + x^2)^{5/2}}. \quad (90)$$

(b) K_5^c

Upon using the integral representation of $K_1(rt)$ and the same procedure as for integral K_4^c to evaluate K_5^c , we obtain

$$K_5^c = \frac{\pi r}{2(x^2 + r^2)^{\frac{3}{2}}}. \quad (91)$$

(c) K_4^s

This integral can be evaluated in the same manner as for K_5^c . We obtain

$$K_4^s = \frac{\pi x}{2(x^2 + r^2)^{\frac{3}{2}}}. \quad (92)$$

Collecting the integrals evaluated up to this point and expressing explicitly in terms of x and r , we find

$$\begin{aligned} (\hat{\mathbf{v}}_x)_{\text{acme}} &\equiv -K_4^c + \frac{r}{2}K_5^c - \frac{1}{\sqrt{2}\xi}K_4^s \\ &= -\frac{\pi}{2\sqrt{2}\xi} \frac{x}{(x^2 + r^2)^{\frac{3}{2}}} \\ &\quad - \frac{\pi}{2(x^2 + r^2)^{1/2}} + \frac{\pi r^2}{4(x^2 + r^2)^{\frac{3}{2}}} + \frac{\pi(2x^2 - r^2)}{2(x^2 + r^2)^{5/2}}. \end{aligned} \quad (93)$$

This contribution of $(\hat{\mathbf{v}}_x)_{\text{acme}}$ to $\hat{\mathbf{v}}_x$ represents the fully deterministic part of the hydrodynamic velocity that is not associated with the Brownian motion of particles giving rise to the dissipative part of the local body force. In fact, some of these terms are independent of the field, but $(\hat{\mathbf{v}}_x)_{\text{acme}}$ is divergent at the origin. This divergence, which is an exact result for the integrals partly making up $\hat{\mathbf{v}}_x(x, r, 0)$, puts Wilson's result for the electrophoresis effect in a rather vexing situation, which necessitates careful examination of the flow profiles obtained of electrolyte solutions before calculating the electrophoretic effect from them.

2. Integrals Evaluated by Means of Contour Integration Methods

There are six integrals whose integrands not only are singular, but also involve rather complicated functions and arguments for the Bessel functions $K_0(\lambda_l \rho)$ ($l = 1, 2, 3$) in the expression for the formal Fourier transform solution for the velocity. They defy conventional evaluation methods, but, fortunately, methods of contour integration may be employed for their evaluation.

To devise methods of contour integration it is necessary to learn about the mathematical properties of the integrals involved. We list their relevant properties below:

(1) The zeros of the arguments of the Bessel function $K_\nu(\lambda_l \rho)$ for $\rho \neq 0$ are found to be:

$$\alpha = \pm i \sqrt{\kappa^2 + \mu'^2} \quad \text{for } \lambda_1 \quad \text{or, when reduced, } t = \pm i \sqrt{2(1 + \xi^2)} \quad \text{for } \omega_1, \quad (94)$$

$$\alpha = 0 \quad \text{for } \lambda_2 \quad \text{or } t = 0 \quad \text{for } \omega_2, \quad (95)$$

$$\alpha = \pm i \frac{\kappa}{\sqrt{2}} \quad \text{for } \lambda_3 \quad \text{or } t = \pm i \quad \text{for } \omega_3. \quad (96)$$

The argument of $K_\nu(\lambda_1 \rho)$ has branch points at $\alpha = \pm i \sqrt{\kappa^2 + \mu'^2}$, whereas the argument of $K_\nu(\lambda_2 \rho)$ has branch points at $\alpha = 0$ and $-\infty$ and the argument of $K_\nu(\lambda_3 \rho)$ has branch points at $\alpha = \pm i \kappa / \sqrt{2}$.

Thus we may insert a branch cut on the imaginary axis of α plane between $\alpha = i \sqrt{\kappa^2 + \mu'^2}$ and $\alpha = -i \sqrt{\kappa^2 + \mu'^2}$ for the integral of $K_\nu(\lambda_1 \rho)$, while a branch cut may be inserted along the negative real axis for the integral of $K_\nu(\lambda_2 \rho)$, and on the imaginary axis between $\alpha = i \kappa / \sqrt{2}$ and $\alpha = -i \kappa / \sqrt{2}$ for the integral of $K_\nu(\lambda_3 \rho)$, respectively. See Figs 2–4 below.

(2) We recall that Bessel function $K_\nu(z)$ of complex variable z is regular in z plane cut along negative real axis.^{28,34} That is, the Bessel function is a multi-valued function in the cut plane. In the present case, $K_0(\lambda_1 \rho)$ changes discontinuously as the branch cut $[-i \sqrt{\kappa^2 + \mu'^2}, i \sqrt{\kappa^2 + \mu'^2}]$ is crossed, whereas $K_\nu(\lambda_2 \rho)$ changes discontinuously as the negative real axis is crossed, and $K_\nu(\lambda_3 \rho)$ changes discontinuously as the branch cut $[-i \frac{1}{\sqrt{2}} \kappa, i \frac{1}{\sqrt{2}} \kappa]$ is crossed on the imaginary axis. Note that the Bessel functions $K_\nu(\lambda_2 \rho)$ and $K_\nu(\alpha \rho)$ are defined in α plane cut along the negative real axis.

(3) We also observe that all the integrands of the singular integrals in I_c and I_s in Eqs. (61) and (62) are even with respect to α .

(4) Moreover, for $0 < \arg \alpha < \pi$ we find

$$-\left(\frac{\pi}{2} - \delta\right) < \arg \lambda_l < \left(\frac{\pi}{2} - \delta\right) \quad \left(\frac{\pi}{2} > \delta > 0; l = 1, 2, 3\right). \quad (97)$$

Therefore in the upper half plane of complex α

$$\lim_{|\alpha| \rightarrow \infty} K_\nu(\lambda_l \rho) = \lim_{|\alpha| \rightarrow \infty} \sqrt{\frac{\pi}{2\lambda_l \rho}} e^{-\lambda_l \rho} \rightarrow 0. \quad (98)$$

By this, if contours for the singular integrals are taken along an infinite semicircle in the upper α plane, Jordan's lemma²⁹ for contour integration along a circle of infinite radius is assuredly satisfied.

(5) Lastly, all the integrands in Eqs. (80)–(82) and (85)–(87) have simple poles at

$$\alpha = \pm \frac{\kappa^2}{2\mu'} \quad \text{or} \quad t = \pm \frac{1}{\sqrt{2\xi}}. \quad (99)$$

There is also a branch cut between $t = -\frac{1}{\sqrt{2\xi}}$ and $t = \frac{1}{\sqrt{2\xi}}$, but this particular branch cut associated with $\sqrt{1 - 2\xi^2 t^2}$ does not play a role in the contour integrals considered in the present work, because the real axis is not crossed by the contours in performing integrations.

All these properties (1)–(5) together suggest it is possible to evaluate the integrals by using methods of contour integration²⁹ along the closed contours of infinite semicircle as depicted in Figs. 2–4. This is indeed a fortunate combination of properties of the integrands involved. We will indicate which contour applies to which integral at appropriate points in the discussion. Since methods of integration will be similar for the integrals involved in K_l^c and K_l^s ($l = 1, 2, 3$) we will illustrate them with the examples of integrals in K_1^c and K_1^s in Appendix A. The results for the rest of integrals will be simply presented with appropriate comments on the use of contours in Figs. 2–4 and useful points if needed. And then by combining the results for the integrals the final formula for the axial and transversal velocities and pressure will be presented. Incidentally, the same contours can be used for evaluating the Fourier transforms for the pair distributions and potentials in Eq. (5)–(8) as shown for completeness in Appendix A.

(d) K_1^c and K_1^s

As prototypes of contour integrals appearing in present work, integrals K_1^c and K_1^s are explicitly evaluated in Appendix A. Integrals K_1^c and K_1^s both have simple poles at $t = \pm (\sqrt{2}\xi)^{-1}$. There is a branch cut along the imaginary axis between $t = -i\sqrt{2(1+\xi^2)}$ and $+i\sqrt{2(1+\xi^2)}$ and also a branch cut on the real axis between $t = -1/\sqrt{2}\xi$ and $t = +1/\sqrt{2}\xi$, but the latter branch cut plays no role in integration since the path of integration in all the contours does not cross it. For this reason the latter branch cut is not shown in Figs. 2–4. For evaluation of both K_1^c and K_1^s the contour in Fig. 2 is used. The results are as follows:

$$K_1^c = -\frac{\sqrt{2}\pi(1+2\xi^2)}{8\xi^3} \sin\left(\frac{x}{\sqrt{2}\xi}\right) K_0(\bar{\omega}r) - \frac{\pi}{2} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-xy} (1 - y^2 + \sqrt{1+2\xi^2 y^2})}{1+2\xi^2 y^2} I_0(\bar{\omega}_1 r), \quad (100)$$

and

$$K_1^s = \frac{\pi(1+2\xi^2)}{8\xi^4} \cos(xt) K_0(\bar{\omega}r) - \frac{\pi}{2} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-xy} y (1 - y^2 + \sqrt{1+2\xi^2 y^2})}{(1+2\xi^2 y^2) (1 + \sqrt{1+2\xi^2 y^2})} I_0(\bar{\omega}_1 r). \quad (101)$$

The integrals in these formulas arise from integration along the branch cut. See Appendix A for the details of calculation. Therefore

$$\begin{aligned} \frac{1}{2} K_1^c + \frac{\xi}{\sqrt{2}} K_1^s &= -\frac{\pi(1+2\xi^2)}{8\sqrt{2}\xi^3} \left[\sin\left(\frac{x}{\sqrt{2}\xi}\right) - \cos(xt) K_0(\bar{\omega}r) \right] K_0(\bar{\omega}r) \\ &\quad - \frac{\pi}{4} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-xy} (1 - y^2 + \sqrt{1+2\xi^2 y^2})}{1+2\xi^2 y^2} \times \\ &\quad \left[1 - \frac{\sqrt{2}\xi y}{(1 + \sqrt{1+2\xi^2 y^2})} \right] I_0(\bar{\omega}_1 r). \end{aligned} \quad (102)$$

(e) K_2^c and K_2^s

For evaluation of these integrals the contour in Fig. 3 is used since the inte-

grand does not have a branch cut on the imaginary axis, but there is contributions from the residues. They give rise to the following results:

$$K_2^c = -\frac{\sqrt{2}\pi(1+2\xi^2)}{8\xi^3} \sin\left(\frac{x}{\sqrt{2}\xi}\right) K_0(\bar{\omega}r), \quad (103)$$

$$K_2^s = \frac{\pi(1+2\xi^2)}{8\xi^4} \cos\left(\frac{x}{\sqrt{2}\xi}\right) K_0(\bar{\omega}r). \quad (104)$$

Therefore we obtain

$$\frac{1}{2}K_2^c + \frac{\xi}{\sqrt{2}}K_2^s = -\frac{\pi(1+2\xi^2)}{8\sqrt{2}\xi^3} \left[\sin\left(\frac{x}{\sqrt{2}\xi}\right) - \cos\left(\frac{x}{\sqrt{2}\xi}\right) \right] K_0(\bar{\omega}r). \quad (105)$$

(f) K_3^c and K_3^s

The integrands of these integrals involve a branch cut along the imaginary axis from $z = -i$ to $+i$. Therefore the appropriate contour to use is \mathcal{C}_3 depicted in Fig. 4. The results of their evaluation are as follows:

$$K_3^c = -\frac{\sqrt{2}\pi}{16\xi^5} (1+2\xi^2) K_0(\bar{\omega}r) \sin\left(\frac{x}{\sqrt{2}\xi}\right) + \frac{\pi}{2} \int_0^1 dy \frac{e^{-xy}y^2(1-y^2)}{1+2\xi^2y^2} I_0(\bar{\omega}_3r), \quad (106)$$

$$K_3^s = \frac{\pi}{8\xi^4} (1+2\xi^2) K_0(\bar{\omega}r) \cos\left(\frac{x}{\sqrt{2}\xi}\right) - \frac{\pi}{2} \int_0^1 dy \frac{e^{-xy}y(1-y^2)}{1+2\xi^2y^2} I_0(\bar{\omega}_3r). \quad (107)$$

Therefore we find

$$-2\xi^2 K_3^c - \sqrt{2}\xi K_3^s = \frac{\pi}{4\sqrt{2}\xi^3} (1+2\xi^2) K_0(\bar{\omega}r) \left[\sin\left(\frac{x}{\sqrt{2}\xi}\right) - \cos\left(\frac{x}{\sqrt{2}\xi}\right) \right] - \frac{\pi}{2} \int_0^1 dy \frac{e^{-xy}\sqrt{2}\xi y(1-y^2)(\sqrt{2}\xi y - 1)}{1+2\xi^2y^2} I_0(\bar{\omega}_3r). \quad (108)$$

Summary for the Reduced Axial Velocity

Collecting the results presented earlier, we obtain the reduced axial velocity

$$\begin{aligned}
\hat{\mathbf{v}}_x(x, \rho, 0) = & -\frac{\pi}{2\sqrt{2}\xi} \frac{x}{(x^2 + r^2)^{3/2}} \\
& - \frac{\pi}{2(x^2 + r^2)^{1/2}} + \frac{\pi r^2}{4(x^2 + r^2)^{3/2}} + \frac{\pi(2x^2 - r^2)}{2(x^2 + r^2)^{5/2}} \\
& - \frac{\pi}{4} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-xy} (1 - y^2 + \sqrt{1 + 2\xi^2 y^2})}{1 + 2\xi^2 y^2} \times \\
& \quad \left[1 - \frac{\sqrt{2}\xi y}{(1 + \sqrt{1 + 2\xi^2 y^2})} \right] I_0(\bar{\omega}_1 r) \\
& - \frac{\pi}{2} \int_0^1 dy \frac{e^{-xy} \sqrt{2}\xi y (1 - y^2)}{1 + 2\xi^2 y^2} [\sqrt{2}\xi y - 1] I_0(\bar{\omega}_3 r). \quad (109)
\end{aligned}$$

We note that the terms made up of trigonometric functions in Eqs. (102), (105), and (108) cancel each other out. This velocity formula (109) is the velocity profile of the countercurrent of the ion atmosphere in the coordinate system fixed at the center ion of the ion atmosphere pulled by the external electric field. The first four terms on the right represent a “deterministic” part of the velocity $(\hat{\mathbf{v}}_x)_{\text{acme}}$ and the two integrals involving the Bessel functions $I_0(\bar{\omega}_1 r)$ and $I_0(\bar{\omega}_3 r)$ stem from the Brownian motion part of the local force—namely, the dressed-up part of the force arising from the interaction of the ion atmosphere and the external electric field.

B. Transversal Velocity

On reducing the integrals, we obtain the reduced transversal velocity as

$$\begin{aligned}
\hat{\mathbf{v}}_\rho(x, \rho, 0) = & \frac{\xi}{2\sqrt{2}} (J_1^c + J_2^c - 2J_3^c) - \frac{1}{\sqrt{2}\xi} J_4^c \\
& - \frac{1}{2} (J_1^s + J_2^s - 4\xi^2 J_3^s) + J_4^s - \frac{1}{2} r J_5^s, \quad (110)
\end{aligned}$$

where the component integrals are defined by

$$J_1^c = \int_0^\infty dt \cos(t\bar{x}) \frac{t^2 \omega_1}{(1 - 2\xi^2 t^2)(1 + R)} K_1(\omega_1 r), \quad (111)$$

$$J_2^c = \int_0^\infty dt \cos(t\bar{x}) \frac{t^2 \omega_1}{(1 - 2\xi^2 t^2)(1 - R)} K_1(\omega_2 r), \quad (112)$$

$$J_3^c = \int_0^\infty dt \cos(t\bar{x}) \frac{t^2}{(1 - 2\xi^2 t^2)} \omega_3 K_1(\omega_3 r), \quad (113)$$

$$J_4^c = \int_0^\infty dt \cos(t\bar{x}) t K_1(tr), \quad (114)$$

and

$$J_1^s = \int_0^\infty dt \sin(t\bar{x}) \frac{t \omega_1}{(1 - 2\xi^2 t^2)} K_1(\omega_1 r), \quad (115)$$

$$J_2^s = \int_0^\infty dt \sin(t\bar{x}) \frac{t \omega_2}{(1 - 2\xi^2 t^2)} K_1(\omega_2 r), \quad (116)$$

$$J_3^s = \int_0^\infty dt \sin(t\bar{x}) \frac{t^3 \omega_3}{(1 - 2\xi^2 t^2)} K_1(\omega_3 r), \quad (117)$$

$$J_4^s = \int_0^\infty dt \sin(t\bar{x}) t^2 K_1(rt), \quad (118)$$

$$J_5^s = \int_0^\infty dt \sin(t\bar{x}) t K_0(rt). \quad (119)$$

These integrals can be evaluated in the same manner as for the axial velocity despite the fact that most of them are given in terms of Bessel functions one order higher than $K_0(z)$ appearing in the axial velocity integrals, namely, $K_1(z)$. The integrals J_l^c and J_l^s for $l = 1, 2, 3$ are evaluated by using the contours in Figs. 2, 3, and 4, respectively, and integrals J_4^c , J_4^s , and J_5^s are evaluated by the conventional method using the integral representation of $K_1(z)$. The results are

as follows:

$$J_1^c = -\frac{\pi(2\xi^2+1)}{8\sqrt{2}\xi^5} K_1(\bar{\omega}r) \sin\left(\frac{x}{\sqrt{2}\xi}\right) + \frac{\pi}{2} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-xy} y^2 \bar{\omega}_1 I_1(\bar{\omega}_1 r)}{(1+2\xi^2 y^2) \left(1 + \sqrt{1+2\xi^2 y^2}\right)}, \quad (120)$$

$$J_2^c = -\frac{\pi}{8\sqrt{2}\xi^5} (2\xi^2+1) K_1(\bar{\omega}r) \sin\left(\frac{x}{\sqrt{2}\xi}\right), \quad (121)$$

$$J_3^c = -\frac{\pi}{8\sqrt{2}\xi^5} (2\xi^2+1) K_1(\bar{\omega}r) \sin\left(\frac{x}{\sqrt{2}\xi}\right) + \frac{\pi}{2} \int_0^1 dy e^{-xy} \frac{y^2(1-y^2)}{(1+2\xi^2 y^2)} I_1(\bar{\omega}_3 r), \quad (122)$$

$$J_4^c = \frac{\pi}{2r^2(u^2+1)^{\frac{3}{2}}} = \frac{\pi r}{2(x^2+r^2)^{\frac{3}{2}}}. \quad (123)$$

Similarly, we obtain

$$J_1^s = \frac{\pi}{8\xi^4} (2\xi^2+1) K_1(\bar{\omega}r) \cos\left(\frac{x}{\sqrt{2}\xi}\right) - \frac{1}{2}\pi \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-xy} y \bar{\omega}_1}{1+2\xi^2 y^2} I_1(\bar{\omega}_1 r), \quad (124)$$

$$J_2^s = \frac{\pi}{8\xi^4} (2\xi^2+1) K_1(\bar{\omega}r) \cos\left(\frac{x}{\sqrt{2}\xi}\right), \quad (125)$$

$$J_3^s = \frac{\pi}{16\xi^6} (2\xi^2+1) K_1(\bar{\omega}r) \cos\left(\frac{x}{\sqrt{2}\xi}\right) + \frac{1}{2}\pi \int_0^1 dy e^{-xy} \frac{y^3 \bar{\omega}_3}{1+2\xi^2 y^2} I_1(\bar{\omega}_3 r), \quad (126)$$

$$J_4^s = -\frac{3\pi x(x^4 - x^2 r^2 - r^4)}{2r^3(x^2 + r^2)^{\frac{5}{2}}}, \quad (127)$$

$$J_5^s = \frac{\pi x}{2(x^2 + r^2)^{3/2}}. \quad (128)$$

In summary, we obtain the reduced transversal velocity

$$\begin{aligned} \hat{\mathbf{v}}_\rho(x, \rho, 0) = & -\frac{\pi r}{2\sqrt{2}\xi(x^2 + r^2)^{\frac{3}{2}}} - \frac{\pi x}{2(x^2 + r^2)^{3/2}} \left[\frac{r}{2} + \frac{3(x^4 - x^2 r^2 - r^4)}{r^3(x^2 + r^2)} \right] \\ & + \frac{\pi}{4} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-xy} y \bar{\omega}_1}{(1+2\xi^2 y^2)} \left(1 + \frac{\sqrt{2}\xi y}{2(1 + \sqrt{1+2\xi^2 y^2})} \right) I_1(\bar{\omega}_1 r) \\ & + \pi \xi^2 \int_0^1 dy e^{-xy} \frac{y^2(y - \sqrt{2}\xi)(1-y^2)}{1+2\xi^2 y^2} I_1(\bar{\omega}_3 r). \end{aligned} \quad (129)$$

As is the case for the axial velocity, the trigonometric function terms in Eqs. (120)–(122) and Eqs. (124)–(126) cancel in the formula for the transversal velocity formula. As is evident from this expression, the transversal velocity also diverges at the origin similarly to the axial velocity does.

C. Pressure

The expression for nonequilibrium pressure $\Delta p = p - p_0$ also can be decomposed into various reduced integrals for the purpose of evaluation:

$$\Delta \hat{p} = \frac{1}{2} (P_1^s + P_2^s) - 2\xi^2 P_3^s - P_4^s - \frac{\xi}{\sqrt{2}} (P_1^c + P_2^c) + \sqrt{2}\xi P_3^c, \quad (130)$$

where $\Delta \hat{p}$ is the reduced pressure

$$\Delta \hat{p} = \Delta p \left(\frac{zeX\kappa^2}{4\pi^2} \right)^{-1} \quad (131)$$

and

$$P_1^c = \int_0^\infty dt \cos(tx) \frac{t^2}{(1 - 2\xi^2 t^2)} K_0(\omega_1 r), \quad (132)$$

$$P_2^c = \int_0^\infty dt \cos(tx) \frac{t^2}{(1 - 2\xi^2 t^2)} K_0(\omega_2 r), \quad (133)$$

$$P_3^c = \int_0^\infty dt \cos(tx) \frac{t^2}{(1 - 2\xi^2 t^2)} K_0(\omega_3 r), \quad (134)$$

$$P_1^s = \int_0^\infty dt \sin(tx) \frac{t(1 + R)}{(1 - 2\xi^2 t^2)} K_0(\omega_1 r), \quad (135)$$

$$P_2^s = \int_0^\infty dt \sin(tx) \frac{t(1 - R)}{(1 - 2\xi^2 t^2)} K_0(\omega_2 r), \quad (136)$$

$$P_3^s = \int_0^\infty dt \sin(tx) \frac{t^3}{(1 - 2\xi^2 t^2)} K_0(\omega_3 r), \quad (137)$$

$$P_4^s = \int_0^\infty dt t \sin(tx) K_0(rt). \quad (138)$$

These integrals are evaluated similarly to the velocities presented earlier:

$$P_1^c = -\frac{\pi}{4\sqrt{2}\xi^3} K_0(\bar{\omega}r) \sin\left(\frac{x}{\sqrt{2}\xi}\right) + \frac{\pi}{2} \int_0^{\sqrt{2(1+\xi^2)}} dy e^{-xy} \frac{y^2}{1+2\xi^2 y^2} I_0(\bar{\omega}_1 r), \quad (139)$$

$$P_2^c = -\frac{\pi}{4\sqrt{2}\xi^3} K_0(\bar{\omega}r) \sin\left(\frac{x}{\sqrt{2}\xi}\right), \quad (140)$$

$$P_3^c = -\frac{\pi}{4\sqrt{2}\xi^3} K_0(\bar{\omega}r) \sin\left(\frac{x}{\sqrt{2}\xi}\right) + \frac{\pi}{2} \int_0^1 dy e^{-xy} \frac{y^2}{1+2\xi^2 y^2} I_0(\bar{\omega}_3 r), \quad (141)$$

$$P_1^s = \frac{\pi}{4\xi^2} K_0(\bar{\omega}r) \cos\left(\frac{x}{\sqrt{2}\xi}\right) - \frac{\pi}{2} \int_0^{\sqrt{2(1+\xi^2)}} dy e^{-xy} \frac{y(1+\sqrt{1+2\xi^2 y^2})}{1+2\xi^2 y^2} I_0(\bar{\omega}_1 r), \quad (142)$$

$$P_2^s = \frac{\pi}{4\xi^2} K_0(\bar{\omega}r) \cos\left(\frac{x}{\sqrt{2}\xi}\right), \quad (143)$$

$$P_3^s = \frac{\pi}{8\xi^4} K_0(\bar{\omega}r) \cos\left(\frac{x}{\sqrt{2}\xi}\right) + \frac{\pi}{2} \int_0^1 dy e^{-xy} \frac{y^3}{1+2\xi^2 y^2} I_0(\bar{\omega}_3 r), \quad (144)$$

$$P_4^s = \frac{\pi x}{2r^3(1+u^2)^{3/2}} = \frac{\pi x}{2(x^2+r^2)^{3/2}}. \quad (145)$$

Collecting these results, we obtain the nonequilibrium pressure profile:

$$\Delta\hat{p} = -\frac{\pi x}{2(x^2+r^2)^{3/2}} - \frac{\pi}{4} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-xy} y(1+\sqrt{2}\xi y + \sqrt{1+2\xi^2 y^2})}{1+2\xi^2 y^2} I_0(\bar{\omega}_1 r) + \frac{\pi}{2} \int_0^1 dy \frac{e^{-xy} \sqrt{2}\xi y^2(1-\sqrt{2}\xi y)}{1+2\xi^2 y^2} I_0(\bar{\omega}_3 r), \quad (146)$$

This shows that $\Delta\hat{p}$ is also singular at the origin of the coordinates. It is significant to observe that the nonequilibrium pressure Δp is generally negative, that is, there is a tension that becomes negative infinite at the origin. This means

the nonequilibrium pressure is compressional. It seems to be a remarkable result, probably deserving a deeper consideration. We will report on a further study of this nonequilibrium pressure separately.

By this, we have now shown that the formal solution of the NS equation of a binary strong electrolyte in an external electric field can be expressed in terms of elementary functions and well-behaved quadratures of regular Bessel functions of second kind $I_\nu(\overline{\omega}_l r)$ ($l = 1, 3$) for all values of x and r . These results show how the axial and transversal (radial) velocity and the nonequilibrium pressure are distributed in the (x, r) space. In other words, they are velocity and pressure distributions around the ions flowing in the medium subjected to an external electric field of an arbitrary strength. They are hitherto unknown results in hydrodynamics of electrolyte solutions. By using these profiles of velocities and nonequilibrium pressure we will be able to deduce, in a well-defined manner, numerous hydrodynamic consequences of ionic motions in the medium in an electric field, subjected to irreversible thermodynamic principles.

D. Transformation of Velocity to Spherical Coordinates

In this work, the NS equation has been solved in cylindrical coordinates for the reason that the external field has an axial symmetry, and hence the velocity and pressure formulas are given in cylindrical coordinates. On the other hand, the ions are regarded as either point charges or hard spheres with spherical symmetry. To examine the motion of the medium around the charges (e.g., hard spheres) it is convenient to have the velocity expressed in coordinates adapted to the symmetry of ions, namely, spherical coordinates. Therefore, it is necessary to transform the velocity vector in cylindrical coordinates to that expressed in spherical coordinates. This aim can be achieved with appropriate transformations for the velocity in cylindrical coordinates (x, r, θ) to that in

spherical coordinates (R, ϑ, φ) , which are related to each other by the equations

$$\begin{aligned}\theta &= \varphi, \\ x &= R \cos \vartheta, \\ r &= R \sin \vartheta,\end{aligned}\tag{147}$$

where R is the radial coordinate, ϑ is the polar angle, and φ is the azimuthal angle of the spherical coordinate system. It should be noted that the roles of x and z are switched from the conventional usage. Accompanying these transformations, the unit vectors are related to each other as follows:

$$\begin{aligned}\boldsymbol{\delta}_x &= \cos \vartheta \boldsymbol{\delta}_R - \sin \vartheta \boldsymbol{\delta}_\vartheta, \\ \boldsymbol{\delta}_r &= \sin \vartheta \boldsymbol{\delta}_R + \cos \vartheta \boldsymbol{\delta}_\vartheta, \\ \boldsymbol{\delta}_\theta &= \boldsymbol{\delta}_\varphi,\end{aligned}\tag{148}$$

where $\boldsymbol{\delta}_x$, $\boldsymbol{\delta}_r$, and $\boldsymbol{\delta}_\theta$ are unit vectors in cylindrical coordinates whereas $\boldsymbol{\delta}_R$, $\boldsymbol{\delta}_\vartheta$, and $\boldsymbol{\delta}_\varphi$ are unit vectors in spherical coordinates corresponding to coordinates R , ϑ , and φ . Since the velocity is decomposable in the two coordinate systems as

$$\hat{\mathbf{v}} = \hat{\mathbf{v}}_x \boldsymbol{\delta}_x + \hat{\mathbf{v}}_\rho \boldsymbol{\delta}_r + (0) \boldsymbol{\delta}_\theta \quad \text{in cylindrical coordinates,}\tag{149}$$

$$= \hat{\mathbf{v}}_R \boldsymbol{\delta}_R + \hat{\mathbf{v}}_\vartheta \boldsymbol{\delta}_\vartheta + (0) \boldsymbol{\delta}_\varphi \quad \text{in spherical coordinates,}\tag{150}$$

where $\hat{\mathbf{v}}_R$ and $\hat{\mathbf{v}}_\vartheta$ are velocity components in spherical coordinates, using the relations in Eq. (148) we obtain the relations between velocity components in two coordinate systems:

$$\hat{\mathbf{v}}_R = \cos \vartheta \hat{\mathbf{v}}_x + \sin \vartheta \hat{\mathbf{v}}_\rho,\tag{151}$$

$$\hat{\mathbf{v}}_\vartheta = -\sin \vartheta \hat{\mathbf{v}}_x + \cos \vartheta \hat{\mathbf{v}}_\rho.\tag{152}$$

Thus multiplying $\hat{\mathbf{v}}_R$ with $(-2\sqrt{2}\xi/\pi)$

$$\mathbf{v}_R = -\frac{2\sqrt{2}\xi}{\pi} \hat{\mathbf{v}}_R,\tag{153}$$

we obtain the radial component of the velocity in spherical coordinates:

$$\begin{aligned} \mathbf{v}_R = & \frac{(\cos \vartheta + \sin \vartheta) \sin \vartheta}{R^2} + \frac{\sqrt{2}\xi}{R} \left[\cos \vartheta \left(1 - \frac{\sin^2 \vartheta}{2} \right) + \frac{\sin^2 \vartheta}{\sqrt{2}R} \right. \\ & \left. - \frac{\cos \vartheta (2 \cos^2 \vartheta - \sin^2 \vartheta)}{R^2} + \frac{3 \sin \vartheta (\cos^4 \vartheta - \cos^2 \vartheta \sin^2 \vartheta - \sin^4 \vartheta)}{R^5} \right] \\ & + 2\sqrt{2}\xi [\cos \vartheta \Theta(R, \vartheta; \xi) - \sin \vartheta \Theta_t(R, \vartheta, \xi)], \end{aligned} \quad (154)$$

where

$$\begin{aligned} \Theta = & \frac{1}{4} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-yR \cos \vartheta} (1 - y^2 + \sqrt{1 + 2\xi^2 y^2})}{1 + 2\xi^2 y^2} \times \\ & \left[1 - \frac{\sqrt{2}\xi y}{(1 + \sqrt{1 + 2\xi^2 y^2})} \right] I_0(\bar{\omega}_1 R \sin \vartheta) \\ & + \frac{1}{2} \int_0^1 dy \frac{e^{-yR \cos \vartheta} \sqrt{2}\xi y (1 - y^2) (\sqrt{2}\xi y - 1)}{1 + 2\xi^2 y^2} I_0(\bar{\omega}_3 R \sin \vartheta), \end{aligned} \quad (155)$$

$$\begin{aligned} \Theta_t = & \frac{1}{4} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-yR \cos \vartheta} y (1 - y^2 + \sqrt{1 + 2\xi^2 y^2})}{(1 + 2\xi^2 y^2)} \times \\ & \left(1 + \frac{\xi y}{\sqrt{2} (1 + \sqrt{1 + 2\xi^2 y^2})} \right) I_1(\bar{\omega}_1 R \sin \vartheta) \\ & + \xi^2 \int_0^1 dy \frac{e^{-yR \cos \vartheta} y^2 (y - \sqrt{2}\xi) (1 - y^2)}{1 + 2\xi^2 y^2} I_1(\bar{\omega}_3 R \sin \vartheta). \end{aligned} \quad (156)$$

These formulas may be used to calculate the force on the center ion of ion atmosphere in the external field. It is closely related to the electrophoretic effect we will need for study of conductance.

In Fig. 5 and Fig. 6, the radial velocity profile \mathbf{v}_R is presented for two cases of ξ to show the behavior of the countercurrent in spherical coordinates. In this contour map of \mathbf{v}_R , its magnitude decreases as the color changes from red to blue according to the scale shown on the right in the figures. It is, in fact, divergent at the origin, meaning an infinite countercurrent, and gradually decreases along the axial direction ($\vartheta = 0$), but as the angle ϑ increases beyond $\vartheta \approx 40$ in the case of,

for example, $\xi = 0.1$ it becomes negative when $R \lesssim 1$ as is evident from the right-hand corner of Fig. 5. This behavior of the countercurrent does not basically change as the field strength ξ increases as is evident from Fig. 6 for $\xi = 3.0$. The negativity of \mathbf{v}_R arises from the deterministic part $(\mathbf{v})_{\text{acme}}$ defined by Eq. (93), which can be negative, but the Brownian motion part of the contribution $[\cos \vartheta \Theta(R, \vartheta; \xi) - \sin \vartheta \Theta_t(R, \vartheta, \xi)]$ is everywhere positive. This feature is shown in Fig. 7 and Fig. 8, in which the contour maps show structures, but do not show a negative domain. The color code bar on the right of the figures is for the magnitude of the function plotted. In Fig. 9, we show the variation of $\Theta(R, 0; \xi)$ with respect to R and ξ , showing its decreasing tendency with increasing R and also with ξ at a given value of R . These figures qualitatively show in which region of (R, ϑ) the countercurrent is least in magnitude, thus offering a least resistance to the motion of charges pulled by the external electric field. This feature therefore offers a useful insight into studying mobility of ions in the electrolyte solutions in the external electric field that, hopefully, can be made use of in the light of irreversible thermodynamic principles..

V. Relation to the Result by Onsager and Wilson

Having obtained an axial velocity formula as a function of x and r , it is appropriate to see how the axial velocity obtained by Onsager and Wilson²¹ for a special position of $x = r = 0$, namely, the coordinate origin at which the center ion of the ion atmosphere is placed, may be recovered. In particular, it is important to see in what manner Wilson's formula for the electrophoretic effect, $f(\xi)$, defined by the relation

$$v_x(0, 0, 0) = -\frac{zeX\kappa}{6\sqrt{2\pi}\eta_0} f(\xi), \quad (157)$$

should be understood, given the exact velocity profile formula (109). Here $v_x(0, 0, 0)$ is the axial velocity of ion at the origin obtained by evaluating the

integrals in the axial velocity formula (59), or its reduced form in Eq. (75) with Eqs. (76) and (77), on taking $x = 0$ and $r = 0$ in the integrals.

At $x = r = 0$ in Eq. (59), the sine transforms all vanish and the cosine transforms contribute well-behaved integrals except for the integral K_5^c [Eq. (84)], which gives rise to a divergent integral, Eq. (63), as pointed out in Subsec. III.4. In Wilson's dissertation,²¹ provided that the integral K_5^c is ignored, the electrophoretic effect $f(\xi)$ is found given by

$$f(\xi) = 1 + \frac{3}{4\sqrt{2}\xi^3} \left\{ 2\xi^2 \sinh^{-1} \xi + \sqrt{2}\xi - \xi\sqrt{1+\xi^2} - (1+2\xi^2) \tan^{-1}(\sqrt{2}\xi) + (1+2\xi^2) \tan^{-1}\left(\frac{\xi}{\sqrt{1+\xi^2}}\right) \right\}. \quad (158)$$

This formula for the electrophoretic effect is in the foundation of the theory of Wien effect for binary strong electrolytes.¹⁸ In view of the divergent integral mentioned, we would like to see in which manner this formula should be obtained from the general formula for the axial velocity, Eq. (109), that we have derived from the solution of the NS equation.

The difficulty of getting this formula from Eq. (109) resides in the term related to $(\widehat{\mathbf{v}}_x)_{\text{acme}}$ [Eq. (93)]

$$\Phi(x, r; \xi) = \frac{x}{(x^2 + r^2)^{3/2}} + \sqrt{2}\xi \left[\frac{1}{(x^2 + r^2)^{1/2}} - \frac{r^2}{2(x^2 + r^2)^{\frac{3}{2}}} - \frac{2x^2 - r^2}{(x^2 + r^2)^{5/2}} \right], \quad (159)$$

which we have termed the “deterministic” part of the axial velocity $(-\widehat{\mathbf{v}}_x)_{\text{acme}}$ —a terminology given to it because it originates from the non-dissipative part of the body force in contrast to the other terms in the axial velocity, that is, the quadratures in Eq. (109). We have multiplied $\sqrt{2}\xi/\pi$ to this factor because the field strength X must be multiplied to obtain the axial velocity. This function $\Phi(x, r; \xi)$ clearly diverges at the origin of the coordinate system. In other words, the axial velocity profiles never passes through the origin at any value of the field strength ξ because the coordinate origin is a singular point of $\widehat{v}_x(x, r, 0)$;

in other words, the countercurrent is infinite at the origin. Furthermore, by examining the upper bounds of the quadratures, the quadratures in \hat{v}_x exponentially increase with respect to ξ if x is such that $xy \leq \bar{\omega}_1 r$ in the interval $\left[1, \sqrt{2(1+\xi^2)}\right]$ in the large ξ (field strength) limit. This would make the countercurrent very large in magnitude in the interval and thus renders the ionic flow unrealizable. However, there is a set of trajectories of (x, r) for which $xy \geq \bar{\omega}_1 r$ and thus the quadratures are exponentially decreasing as ξ increases; these figures are not shown in this paper for lack of space, but the velocity profiles are instead shown in spherical coordinates in the previous section. Therefore the optimum value of (x, r) must be that of $\min [\hat{v}_x(x, r; \xi)]$ for a given field strength, namely, the trajectory of (x, r) corresponding to the valley of the axial velocity surface. This trajectory $(x, r)_{x=x_c, r=r_c} \in \min [\hat{v}_x(x, r; \xi)]$ can be determined as a function of ξ by a numerical means only. The values of x_c and r_c are $O(1)$ in reduced units of distance or κ^{-1} in actual units. We have already shown in the previous section that this aspect is better displayed if spherical coordinates are employed.

In any case, Wilson's result for $f(\xi)$ can be recovered, *only (1) if the factor $\Phi(x, r; \xi)$ is ignored or the arguments x and r are chosen so that $\Phi(x, r; \xi) = 0$ in the definition of electrophoretic effect and (2) if not only x and r are set equal to zero in the integrals in Eq. (109) for \hat{v}_x , but also the terms therein that arise from the sine transforms are omitted, that is, the second term in the square brackets in Eq. (160) given below.* We explain it more explicitly: First, if we set $x = r = 0$ in the integrals of Eq. (109) we obtain

$$\begin{aligned} \Xi \equiv & -\frac{\pi}{4} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{(1-y^2 + \sqrt{1+2\xi^2 y^2})}{1+2\xi^2 y^2} \left[1 - \frac{\sqrt{2}\xi y}{(1+\sqrt{1+2\xi^2 y^2})} \right] \\ & - \frac{\pi\xi}{\sqrt{2}} \int_0^1 dy \frac{y(1-y^2)}{1+2\xi^2 y^2} [\sqrt{2}\xi y - 1]. \end{aligned} \quad (160)$$

For this we note that

$$I_0(z)|_{z=0} = 1.$$

Furthermore, if the second term in the square brackets in the first and second integrals in Ξ is neglected, that is, the terms $\sqrt{2\xi y}/(1 + \sqrt{1 + 2\xi^2 y^2})$ and 1, the resulting integrals are precisely the integrals Wilson²¹ evaluated to obtain the result for $f(\xi)$ given in Eq. (158):

$$\Xi_W = -\frac{\pi}{2} \left[\frac{1}{2} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{(1 - y^2 + \sqrt{1 + 2\xi^2 y^2})}{1 + 2\xi^2 y^2} + 2\xi^2 \int_0^1 dy \frac{y^2 (1 - y^2)}{1 + 2\xi^2 y^2} \right]. \quad (161)$$

The integrals here are elementary. It is easy to show that Ξ_W indeed gives rise to $f(\xi)$ in Eq. (158).

By this, we see that the connection of $f(\xi)$ to the axial velocity formula in Eq. (109) can be made only when we arbitrarily set $\Phi = 0$ and also $x = 0$ and $r = 0$ in the integrals and when some terms therein originating from the sine transform terms in the axial velocity are dropped arbitrarily.

In any case, in view of the fact that the Onsager–Wilson theory for Wien effect predicts ionic conductances too small in comparison²⁷ with experiment it would be useful to examine whether the complete velocity profile formula would improve the theoretical prediction. Application to the question of electrophoretic factor of the axial velocity formula will be made in the sequel⁴³ where conductivity will be studied in comparison with experiment.

VI. Discussion and Concluding Remarks

Since ions interact with each other through long range Coulombic interactions, and ion atmospheres with ions and the external field, the whole body of the solution collectively and cooperatively moves subjected to the external field. Consequently, the macroscopic behavior of electrolyte solutions in the presence

of an external electric field is not simple.

Their electrical conductivity in particular has attracted a great deal of attention in physical chemistry for reasons related to the basic questions in chemistry and thermodynamics including the behaviors of electrolytic solutions from the early days of physical chemistry. On the basis of Debye’s theory of electrolytic solutions,³⁶ Lars Onsager,^{14,37} in particular, elucidated the physical mechanisms—the electrophoretic effect and the relaxation time effect—underlying the conduction phenomena, which ultimately require solutions of hydrodynamic equations together with appropriate constitutive equations for irreversible nonequilibrium fluxes in terms of thermodynamic forces. The Onsager–Wilson (OW) theory of Wien effect,²¹ and Onsager–Kim (OK) theory³⁸ in the case of asymmetric strong electrolytes, depicts the manner in which nonlinear field effects on ionic conductivity and mobility can be studied. However, critical studies of these theories have not been made in the literature. Even numerical studies of, for example, the OK theory, although difficult, have not been made as yet. The Onsager–Liu theory³⁹ and the Onsager–Chen theory⁴⁰ were the most recent follow-ups in the aforementioned line, but their works were concerned with higher-order density corrections, not the Wien effect itself.

The ionic association theory approach by Patterson and his collaborators⁴¹ using the Bjerrum’s theory⁴² of ionic association and Onsager’s theory of weak electrolytic conduction³⁷ was based on the electrophoretic effect obtained by Wilson despite the question of divergence mentioned earlier. In view of Wilson’s electrophoretic effect factor $f(\xi)$ needing reassessment and probably a revision because of the divergence difficulty mentioned, and the notion of ionic association that probably can be better addressed by means of the modern statistical mechanics of ionic liquids,^{32,33} the approach of Patterson et al. would require a fresh re-examination. Therefore, the theory of Wien effect and more

generally, nonlinear field effects on ionic conductivity of electrolyte solutions is not a closed subject as yet despite its long history in the opinion of the present authors.

At this point, it is useful to reconsider, by using the radial velocity component $\hat{\mathbf{v}}_R$ given in Eq. (154), the connection of the present work to the result for the electrophoretic effect examined with $\hat{\mathbf{v}}_x$ in cylindrical coordinate in Sec. V. Here we would like to consider the radial velocity $\hat{\mathbf{v}}_R$ in the direction parallel to the external field, that is, $\vartheta = 0$, which then reads

$$\mathbf{v}_R(R, 0, \xi) = \frac{\sqrt{2}}{R} \left(1 - \frac{2}{R^2} \right) + 2\sqrt{2}\Theta(R, 0; \xi). \quad (162)$$

Before proceeding further, it is useful to note that if we define a generalized electrophoretic factor $\mathfrak{f}(R, \vartheta, \xi)$ on the basis of the velocity in spherical coordinates $\mathbf{v}(R, \vartheta, \varphi) \equiv \mathbf{v}_x \cos \vartheta + \mathbf{v}_\rho \sin \vartheta$ in analogy to Eq. (157)

$$\mathbf{v}(R, \vartheta, \varphi) = -\frac{zeX\kappa}{6\sqrt{2}\pi\eta_0} \mathfrak{f}(R, \vartheta, \xi), \quad (163)$$

then $\mathbf{v}_R(R, 0, \xi)$ is related to $\mathfrak{f}(R, 0, \xi)$ by the relation

$$\mathbf{v}_R(R, 0, \xi) / \xi = \frac{2\sqrt{2}}{3} \mathfrak{f}(R, 0, \xi). \quad (164)$$

If $R = \sqrt{2}$, $\vartheta = 0$ then

$$\mathbf{v}_R(\sqrt{2}, 0, \xi) / \xi = \frac{2\sqrt{2}}{3} \mathfrak{f}(\sqrt{2}, 0; \xi) = 2\sqrt{2}\Theta(\sqrt{2}, 0; \xi). \quad (165)$$

Note that in the actual distance scale $R = \sqrt{2}$ corresponds to the radial position at $2\kappa^{-1}$, i.e., twice the Debye length, and at this point the factor Φ [Eq. (159)] related to $(\hat{\mathbf{v}}_x)_{\text{acme}}$, the deterministic part of the velocity, vanishes: $(\hat{\mathbf{v}}_x)_{\text{acme}}|_{R=\sqrt{2}, \vartheta=0} = 0$. And the choice of this particular value of $R = \sqrt{2}$ replaces the step by which the divergent integral was arbitrarily discarded in Wilson's procedure. Then the resulting $\mathfrak{f}(\sqrt{2}, 0, \xi)$ is rather similar to $f(\xi)$, which can be shown given by Ξ_W (Eq. (161)). We emphasize that here the

choice of $R = \sqrt{2}$ is guided by $\Phi(R, \vartheta)|_{R=\sqrt{2}, \vartheta=0} = 0$. We will explore its possible irreversible thermodynamics basis in the sequel.

On the other hand, If $\vartheta = 0$ and $R = 1/\sqrt{2}$, i.e., at $\sqrt{2}$ times the Debye length κ^{-1} of the radial position,

$$\mathbf{v}_R(1/\sqrt{2}, 0, \xi) / \xi = \frac{2\sqrt{2}}{3} \mathfrak{f}(1/\sqrt{2}, 0, \xi) = \sqrt{2} (2\Theta(1/\sqrt{2}, 0; \xi) - 1). \quad (166)$$

These two cases are plotted In Fig. 10 and Fig. 11, respectively, with respect to ξ . We notice that $\mathbf{v}_R(1/\sqrt{2}, 0, \xi) / \xi \gg \mathbf{v}_R(\sqrt{2}, 0, \xi) / \xi$, or, put in another way, the countercurrent is much larger in magnitude in the case of $R = 1/\sqrt{2}$ than $R = \sqrt{2}$.

These two cases of $\mathfrak{f}(R, 0, \xi)$ correspond to $f(\xi)$ in Wilson's work, but not equal to $f(\xi)$. Evidently, they are well-behaved and finite functions of ξ , whose behavior is reminiscent of that of $f(\xi)$. Interestingly, $\mathfrak{f}(\sqrt{2}, 0, \xi)$ is closer in magnitude to $f(\xi)$ than $\mathfrak{f}(1/\sqrt{2}, 0, \xi)$. This aspect and the related will be given a more detailed consideration in the sequel⁴³ where application of the results of the present work to the theory of conductance will be examined in detail with the help of the irreversible thermodynamic principles associated with the flow.

The present work was born out of our desire to fully comprehend the meanings of the divergence-causing integral(s) in the formal Fourier transform solution of the NS equation of binary electrolytes in the presence of an external electric field and to find thereby a way to circumvent the divergence in question. In this article, to achieve this goal we have fully evaluated the aforementioned formal solution of the NS equation without assuming a special case of spatial positions, in terms of simple elementary functions plus quadratures of well-behaved functions. What we have obtained are the exact velocity and pressure profiles in space, which we may apply to study irreversible phenomena in the binary electrolyte solutions in the electric field, including electrical conduction phenomena. Being a full exact solution without an approximation, it promises

to provide a more complete picture of conduction phenomena. This part of the study will be made in the sequels to this article.

The solution [Eqs. (109), (129), (146), and (154)] of the NS equation obtained here is a rare example of rather simple, but explicit solutions for the kind of complex, but practical systems, that are amenable to relatively straightforward mathematical analysis and computation by a desktop computer, because the formulas involved are either elementary functions or comparatively simple quadratures free from a singular behavior, such as of poles and other singularities. They therefore appear to be potentially very useful for gaining insights into and describing how ions in electrolyte solutions move in the presence of an external electric field. These insights also should help us develop theories of electrical conductivity and related transport phenomena in systems^{1–13} of current interest in science and engineering, such as plasmas, semiconductors, etc. in electromagnetic fields.

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Appendix A. Examples for Contour Integration of Integrals

In this Appendix, we use Integrals K_1^c and K_1^s [Eqs. (76) and (77)] as typical examples illustrating the methods of contour integration used in this work. Other integrals can be evaluated similarly by using appropriate contours given in Fig. 3 and Fig. 4.

1. Integrals K_1^c and K_1^s

Fig. 2 is used for evaluating this integral. Consider the contour integral along contour \mathcal{C}_1 in complex plane z depicted in Fig. 2

$$\mathcal{C}_1 K_1^c = \int_{\mathcal{C}_1} dz e^{ixz} \frac{\omega_1^2}{1 - 2\xi^2 z^2} K_0(\omega_1 r), \quad (\text{A1})$$

where

$$\omega_1 = \left[1 + z^2 + \sqrt{1 - 2\xi^2 z^2} \right]^{1/2}. \quad (\text{A2})$$

Since there is no singularity enclosed by the contour, this contour integral $\mathcal{C}_1 K_1^c$ is clearly equal to zero. Integral $\mathcal{C}_1 K_1^c$ can be decomposed into integrals along the paths C_- , C_+ , C , C_∞ , and along the real axis t . We thus may write it as

$$\begin{aligned} \mathcal{C}_1 K_1^c &= \int_{-\infty}^{\infty} dt \frac{(1 + t^2 + \sqrt{1 - 2\xi^2 t^2})}{1 - 2\xi^2 t^2} e^{ixt} K_0(\omega_1(t) r) \\ &+ \int_{C_-} dz \frac{(1 + z^2 + \sqrt{1 - 2\xi^2 z^2})}{1 - 2\xi^2 z^2} e^{ixz} K_0(\omega_1(z) r) \\ &+ \int_{C_+} dz \frac{(1 + z^2 + \sqrt{1 - 2\xi^2 z^2})}{1 - 2\xi^2 z^2} e^{ixz} K_0(\omega_1(z) r) \\ &+ \int_C dz \frac{(1 + z^2 + \sqrt{1 - 2\xi^2 z^2})}{1 - 2\xi^2 z^2} e^{ixz} K_0(\omega_1(z) r) \\ &+ \int_{C_\infty} dz \frac{(1 + z^2 + \sqrt{1 - 2\xi^2 z^2})}{1 - 2\xi^2 z^2} e^{ixz} K_0(\omega_1(z) r) \\ &= 0. \end{aligned} \quad (\text{A3})$$

The first integral on the right can be shown to be equal to $2K_1^c$. By the theorem of residues²⁹ the integrals $C_-K_1^c$ and $C_+K_1^c$ gives πi times residue of $(C_\pm K_1^c)$.

Thus we obtain

$$C_-K_1^c + C_+K_1^c = \frac{\sqrt{2}\pi(1+2\xi^2)}{4\xi^3} \sin\left(\frac{x}{\sqrt{2}\xi}\right) K_0(\bar{\omega}r), \quad (\text{A4})$$

where

$$\bar{\omega} = \frac{\sqrt{1+2\xi^2}}{\sqrt{2}\xi}. \quad (\text{A5})$$

To transform the contour integral CK_1^c around the branch cut along the imaginary axis we observe that if the phase of the argument of $K_0(\omega_1 r)$ on the right hand lip of the cut is chosen equal to zero the phase of the argument on the left hand lip is πi , so that the argument has the form $e^{\pi i}\omega_1 r$ for the Bessel function on the left side of contour C . We now observe that the Bessel function can be continued from the left side of the cut to the right side by the following continuation formula²⁸

$$K_0(e^{i\pi}z) = K_0(z) - \pi i I_0(z), \quad (\text{A6})$$

where $I_0(z)$ is the regular solution for the second kind of the Bessel function of order 0, $K_0(z)$ being irregular in contrast to $I_0(z)$ being regular. The irregular Bessel function $K_\nu(z)$ ($\nu \geq 0$) diverges logarithmically as $z \rightarrow 0$. In series representation the Bessel function $I_0(z)$ is given by the formula

$$I_0(z) = \sum_{m=0}^{\infty} \frac{\left(\frac{1}{2}z\right)^{2m}}{(m!)^2}. \quad (\text{A7})$$

This function is finite at $z = 0$, but it behaves asymptotically as

$$I_0(z) \sim (2\pi z)^{-1/2} e^z [1 + O(z^{-1})] \quad (|\arg z| < \pi). \quad (\text{A8})$$

Using formula (A6) and changing variable from iy to y , we obtain

$$CK_1^c = \pi \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-xy} \left(1 - y^2 + \sqrt{1 + 2\xi^2 y^2}\right)}{1 + 2\xi^2 y^2} I_0(\bar{\omega}_1 r), \quad (\text{A9})$$

where

$$\bar{\omega}_1 = \left[1 - y^2 + \sqrt{1 + 2\xi^2 y^2}\right]^{1/2}. \quad (\text{A10})$$

The contour integral along the infinite semicircle C_∞ vanishes identically because $K_0(\omega_1 r)$ vanishes^{28,34} as $|z| \rightarrow \infty$. Collecting the results obtained above into Eq. (A3), we evaluate the integral K_1^c in the form:

$$\begin{aligned} K_1^c = & -\frac{\sqrt{2}\pi(1+2\xi^2)}{8\xi^3} \sin\left(\frac{x}{\sqrt{2}\xi}\right) K_0(\bar{\omega}r) \\ & -\frac{\pi}{2} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-xy} \left(1 - y^2 + \sqrt{1 + 2\xi^2 y^2}\right)}{1 + 2\xi^2 y^2} I_0(\bar{\omega}_1 r). \end{aligned} \quad (\text{A11})$$

The procedure of evaluating integrals K_1^s is entirely parallel to the one presented above for K_1^c with the contour in Fig. 2. The result for the reduced integral is K_1^s

$$\begin{aligned} K_1^s = & \frac{\pi}{8\xi^4} (1 + 2\xi^2) \cos\left(x/\sqrt{2}\xi\right) K_0\left(\omega_1\left(-1/\sqrt{2}\xi\right)r\right) \\ & -\frac{\pi}{2} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-xy} y \left(1 - y^2 + \sqrt{1 + 2\xi^2 y^2}\right)}{(1 + 2\xi^2 y^2) \left(1 + \sqrt{1 + 2\xi^2 y^2}\right)} I_0(\bar{\omega}_1 r). \end{aligned} \quad (\text{A12})$$

The procedures for integrals K_2^c , K_3^c , K_2^s , K_3^s in integrals K_c and K_s are entirely parallel to those presented here for K_1^c and K_1^s if the contours in Fig. 3–4 are made use of.

2. Evaluation of Pair Distribution functions and Potentials

The formal formulas for the pair distribution functions and potentials presented in Sec. II can be evaluated by using the same methods as for the velocity and pressure. In this part of Appendix A, we present the results for them for completeness, although we have not needed them for the purpose of the present paper.

1. Pair distribution Functions

With the definition of the symbol

$$\Delta \hat{f}_{kl} = \left(\frac{n\kappa^3}{2\sqrt{2}\pi^2 z} \right)^{-1} (f_{kl} - n^2) \quad (kl = ii, jj, ij) \quad (\text{A13})$$

we obtain

$$\begin{aligned} \Delta \hat{f}_{ii} = & -\frac{\pi}{2} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-xy} (1 - y^2 + \sqrt{1 + 2\xi^2 y^2})}{1 + 2\xi^2 y^2} I_0(\bar{\omega}_1 r) \\ & - \frac{\pi}{2} \int_0^1 dy e^{-yx} \frac{4y^2 \xi^2}{(1 + 2\xi^2 y^2)} I_0(\bar{\omega}_3 r), \end{aligned} \quad (\text{A14})$$

$$\begin{aligned} \Delta \hat{f}_{jj} = & \frac{\sqrt{2}\pi}{\xi} \sin\left(\frac{x}{\sqrt{2}\xi}\right) K_0(\bar{\omega} r) \\ & + \frac{\pi}{2} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-xy} (1 - y^2 + \sqrt{1 + 2\xi^2 y^2})}{1 + 2\xi^2 y^2} I_0(\bar{\omega}_1 r) \\ & - \frac{\pi}{2} \int_0^1 dy e^{-yx} \frac{4y^2 \xi^2}{(1 + 2\xi^2 y^2)} I_0(\bar{\omega}_3 r), \end{aligned} \quad (\text{A15})$$

and

$$\begin{aligned} \Delta \hat{f}_{ij} = & -\frac{\pi}{2} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-xy} \left[\left(1 + \sqrt{1 + 2\xi^2 y^2}\right) \left(1 \mp \frac{\xi}{\sqrt{2}} y\right) - y^2 \right]}{1 + 2\xi^2 y^2} I_0(\bar{\omega}_1 r) \\ & \pm \frac{\pi}{2} \frac{\xi}{\sqrt{2}} \int_0^1 dy y \frac{2e^{-yx}}{(1 + 2\xi^2 y^2)} I_0(\bar{\omega}_3 r). \end{aligned} \quad (\text{A16})$$

2. Potentials

With the definition of symbols

$$\hat{\psi}_j = \psi_j(\pm \mathbf{r}) \left(\frac{ze\kappa}{\sqrt{2}\pi D} \right)^{-1} = -\psi_i(\mp \mathbf{r}) \left(\frac{ze\kappa}{\sqrt{2}\pi D} \right)^{-1} \quad (\text{A17})$$

we obtain

$$\begin{aligned} \hat{\psi}_j = & -\frac{\pi}{2} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{ye^{-yx} I_0(\bar{\omega}_1 r)}{(1 + 2\xi^2 y^2)} \left(\sqrt{1 + 2\xi^2 y^2} + 1 \mp \sqrt{2}\xi \right) \\ & - \pi \int_0^1 dy y \frac{e^{-yx}}{(1 + 2\xi^2 y^2)} I_0(\bar{\omega}_3 r) \left(1 \mp \sqrt{2}\xi \right). \end{aligned} \quad (\text{A18})$$

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Figure Captions

Fig. 1 The cylindrical coordinate system employed.

Fig. 2 Contour \mathcal{C}_1 for integrals K_1^c and K_1^s . This contour also applies to integrals J_1^c and J_1^s and P_1^c and P_1^s . The bold line denotes the branch cut.

Fig. 3 Contour \mathcal{C}_2 for integrals K_2^c and K_2^s . This contour also applies to integrals J_2^c and J_2^s and P_2^c and P_2^s . The bold line denotes the branch cut.

Fig. 4 Contour \mathcal{C}_3 for integrals K_3^c and K_3^s . This contour also applies to integrals J_3^c and J_3^s and P_3^c and P_3^s . The bold line denotes the branch cut, which is on the negative real axis.

Fig. 5 Contour maps of the radial velocity profile for different field strength in the case of $\xi = 0.1$. The radial velocity becomes singular at the coordinate origin. The magnitude of velocity diminishes from red to blue.

Fig. 6 Contour maps of the radial velocity profile for different field strength in the case of $\xi = 3.0$. The feature of the figure is similar to Fig. 5.

Fig. 7 The scaled radial velocity profile $\Theta(R, \vartheta, \xi)$ in the case of $\xi = 0.1$.

Fig. 8 The scaled radial velocity profile $\Theta(R, \vartheta, \xi)$ in the case of $\xi = 3.0$.

Fig. 9 The cross section of $\Theta(R, \vartheta, \xi)$ at $\vartheta = 0$ plotted against R for different values of ξ . This figure gives an idea of how the $\Theta(R, \vartheta, \xi)$ profiles vary with R and the field strength ξ .

Fig. 10 The scaled radial velocity $\mathfrak{f}(\sqrt{2}, 0, \xi) = \text{at } (R = \sqrt{2}, \vartheta = 0)$ as a function of ξ . This is equivalent to Wilson's electrophoretic factor $f(\xi)$, which is calculated with \mathbf{v}_x in cylindrical coordinates instead of spherical coordinates.

Fig. 11 The scaled radial velocity $\mathfrak{f}(1/\sqrt{2}, 0, \xi) = \text{at } (R = 1/\sqrt{2}, \vartheta = 0)$ as a function of ξ . Comparison of this figure with Fig. 10 gives an idea how the electrophoresis might vary with R .

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Figure 2:

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Figure 3:

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Figure 11:

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